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The Synthesis and Characterization of Novel Platinum and Palladium Diimene Compounds For Use as Anticancer Drugs and CO_2 Reduction Catalyst

A Senior Honors Research Thesis in the
Department of Chemistry
Submitted to the Honors Committee of
Sweet Briar College

By Emma Kate Payne

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in Chemistry
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For my parents, my brother, Papa, and all my friends for understanding and support when I needed it.

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LIST OF ABBREVIATIONS

CO_2- carbon dioxide
Pt- platinum
Pd- palladium
phen- 1,10-phenanthroline
dpk- di(2-pyridyl) ketone
dione- 1,10-phenanthroline-5,6-dione
cisplatin- cis-dichlorodiammineplatinum II
frit- sintered glass Buchner funnel
vac-line- vacuum manifold
bdppz- dipyridophenazine benzoic acid
FT/IR- Fourier Transport/Infrared
GC/MS- Gas Chromatograph/Mass Spectrometer
N_2- nitrogen
gbdppz- glucosified-bdppz
DMF- dimethylformamide
Cl- chlorine
K_2PtCl_6- potassium hexachlorplatinate(IV)
DMSO- dimethylsulfoxide
K_2PdCl_6- potassium hexachloropalladate(IV)
KBr- potassium bromide
HNO_3- nitric acid
HCl- hydrochloric acid
NaOH- sodium hydroxide
THF- tetrahydrofuran
glucosamine- glucosamine hydrochloride
NMR- Nuclear Magnetic Resonance
K_2PdCl_4- potassium tetrachloropalladate(II)
$PdCl_2$- palladium (II) chloride
Ag_2Tartrate- Silver Tartrate
Ag_3Citrate- Silver Citrate
K_2PF_6- potassium hexaflorophosphate
K_2PtCl_4- potassium tetrachloroplatinate(II)
D_20- deuterium oxide
$LiClO_4$- lithium perchlorate

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Synthesis and Development of Palladium (IV) Ligand Anti-Cancer Drugs

Emma Kate Payne
Junior Honors Thesis

Abstract: Different synthesis mechanisms have been attempted for bdppz (benzene-dipyridophenazene), gdppz (glucosified-bdppz), Pd-bdppz, and Pd-gdppz, which are potential anti-cancer drugs. The compound bdppz was synthesized using equimolar amounts of dipyridobenzoquinone (dione) and 3,4-diaminobenzoic acid. The compound gdppz was synthesized using equimolar amounts of bdppz and glucose. Pd-bdppz was synthesized using eqimolar amounts of Pd-dione and 3,4-diaminobenzoic acid. Pd-gdppz was synthesized using equimolar amounts of Pd-bdppz and glucose. Other esters of the bdppz have also been synthesized. These reactions have been conducted using different techniques and solvents. FT/IR, GC/MS, and HPLC data support these synthetic mechanisms and provide evidence for the development of new products. Further experimentation will be conducted during the summer of 2002.

Introduction:

In the early 1980's, many researchers began examining the interactions of octahedrally coordinated complexes of copper, nickel, zinc, iron, cobalt, chromium, rhodium, osmium, and rutheninium with DNA. J. Barton and her coworkers conducted many of the pioneering studies on octahedrally coordinated oganometallic molecular probes.[1] She has investigated the DNA-interactions of many transition metal compounds containing intercalative ligands such as 1,10-phenanthroline. These compounds demonstrated site-specific DNA interaction and some have shown to engage in photolytic strand cleavage. The octahedrally coordinated platinum and palladium family transition metals are absent from this list of transition metal DNA probes.

In the summer of 1996, Dr. Robert Granger developed a new scheme for the synthesis of water-soluble octahedrally coordinated platinum (IV) complexes with intercalative ligands.[2,3] Research continued and focused on the synthesis of Pt(IV) and Pd(IV) complexes of 1,10-phenanthroline and 2,2'-dipyridine. These complexes were found to interact with DNA in a similar fashion to the octahedrally coordinated complexes of other transition metals.

Platinum compounds are widely used medically in chemotherapeutic agents. Cisplatin (cis-diamminedichloroplatinum), a square planar molecule, is commonly used alone or in combination with other chemotherapeutic drugs in the treatment of several aggressive cancers. Resistance to cisplatin, though, can develop and the drug itself is toxic to the patient.

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[1] a) Kumar, C.V.; Barton, J.K.; Turro, N.J. *J. Am. Chem. Soc.*, **1985**, 107, 5518-5523. b) Rehmann, J.P.; Barton, J.K. *Biochemistry* **1990**, 29, 1701-1709. c) Sitlani, A.; Dupureur, C.M.; Barton, J.K. *Journal of the American Chemical Society* **1993**, 115, 12589-12590.

[2] R. Granger *et al.* "Synthesis and Characterization of (1,10-phenanthroline) platinum tetrachloride" *The Virginia Journal of Science*. Vol.? Pp.? **(1999)**

[3] R. Granger *et al.* " The Synthesis and Characterization of tris(1,10-phenanthroline)platinum(IV) hexafluorophosphate" *Polyhedron*. **Submitted June 1999**.

Because of the importance of platinum in anti-cancer drugs, Dr. Robin Davies and Dr. Robert Granger wanted to test the anti-cancer activity of octahedrally coordinated metal center complexes (4+) with intercalative ligands. In the summer of 1997, Dr. Davies began cell culture experiments using Dr. Granger's novel platinum (IV) and palladium (IV) complexes. These complexes proved to be extremely active against malignant cell lines. To date, Dr. Granger has supplied Dr. Davies' research team with four Pt(IV) diimene complexes and two Pd(IV) diimene complexes. Dr. Davies has conducted preliminary cytotoxicity tests on $[Pt(phen)_3]^{4+}$ against chicken and mouse cells, and tested all of them against human leukemia cells. All of the compounds studied have shown bioactivity toward the cancerous cell lines. The palladium compounds proved to be the most toxic, while the $[Pt(dione)(phen)_2]^{4+}$ showed a cytostatic response.

Because of the promising response from these compounds, further investigation was conducted to try to determine exactly how these compounds interact with DNA. Studies conducted by Dr. Granger illustrated that the (4+) charge on these complexes bends the negatively charged DNA strands upon binding. This finding lead to studies by Dr. Granger that focus on synthetic efforts to modify the intercalating ligands of these compounds. Studies have begun to develop a series of extended ligand systems that will be able to insert deeper into the DNA. These extended ligands will hold the metal charge further away from the DNA's backbone, preventing the DNA from bending and promoting an intercalative binding mode.

One potential extended ligand has been developed. The compound, bdppz (benzene-dipyridophenazene), is made when equimolar amounts of dione (dipyridobenzoquinone) and 3,4-diaminobenzoic acid are refluxed. This reaction leads to the addition of two more aromatic rings, which greatly extends the ligand and improves the possibilities that it will intercalate with the DNA. This reaction also leaves a functional group on the end of the ligand, the carboxylic acid group. Other compounds could be attached at this functional group.

One compound that could be attached is glucose. Evidence has shown that cancer cells have a much higher metabolism than normal cells. To accommodate this faster metabolism, cancer cells have adapted mechanisms to actively transport nutrients into the cell. In theory an anti-cancer drug with a nutrient attached, like glucose, would be taken up by the cancer cells more readily than by the normal cells. Glucose could also enhance the solubility properties of the bdppz ligand. With glucose attached, the compound is more likely to be water soluble.[4]

The following information outlines the steps, procedures, and developments of my attempts at creating an extended ligand with a nutrient attached. Attaching the extended ligand to a palladium (IV) metal center has also been attempted. These developments could provide a drug that targets the cancer cells leaving normal cells to continue to develop, which would be effective against cisplatin-resistant tumors.

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[4] Y. Khmelnitsky *et al.* "Synthesis of Water-Soluble Paclitaxel Derivatives by Enzymatic Acylation" *J. Am. Chem. Soc.*, **1997**, 119, 11554-11555.

Experimental:

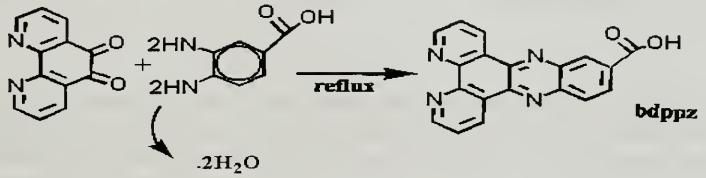
Materials:

1,10-phenanthroline- Aldrich
H_2SO_4 (sulfuric acid)- VWR
HNO_3 (nitric acid)- VWR
KBr (potassium bromide)-Baker
Chloroform- VWR
Magnesium Sulfate- Baker
3,4-diaminobenzoic acid- Aldrich
1,1,1-trichloroethane- VWR
Ethanol- VWR
Glucose- Aldrich
HPLC grade Methanol- Aldrich
Ether- VWR
Acetone- VWR
HPLC grade Acetonitrile- Aldrich
THF (tetrahydrofuran)- VWR
DMF- Aldrich

Instruments:

pH meter- Orion Model 410A
Buchi Rotavapor R-114
FT/IR- 4020 Galaxy Series FT-IR
Gas Chromatograph 5890 Series II Plus- Hewlett-Packard
Mass Spectrometer and Software- Hewlett-Packard
Sep-Pak Cartridge- Waters Corporation Part No.WAT051910

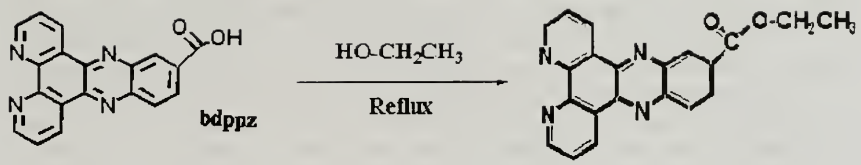
Synthesis of bdppz



The synthesis of 1,10-phenanthroline-5,6-dione (dipyridobenzoquinone)-abbreviated as dione- followed that established by Eisenberg.[5] 3,4- diaminobenzoic acid was sublimed using a cold finger to dispose of the impurities. White, orange crystals formed on the cold finger and were used in the reaction. Equimolar amounts of the sublimed 3,4-diaminobenzoic acid and dione were refluxed for 2 hours in 20 mL of 1,1,1-trichloroethane. A light brown precipitate formed. The 1,1,1-trichloroethane was rotovapped off and the remaining solution was run through a frit and put on the vac-line to dry. All glassware containing the bdppz was wrapped in aluminum foil because this compound is sensitive to light. An FT/IR and GC/MS were taken of the product (Figure 1 and Figure 2).

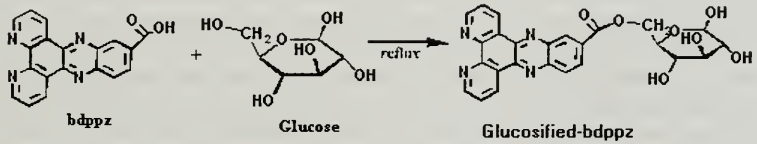
Synthesis of ethyl-bdppz

[5] Eisenberg, Richard *et al.* "Synthesis, Characterization, and Spectroscopy of Dipyridocatecholate Complexes of Platinum". *Inorg. Chem.* **1997,** 36, 2287-2293.



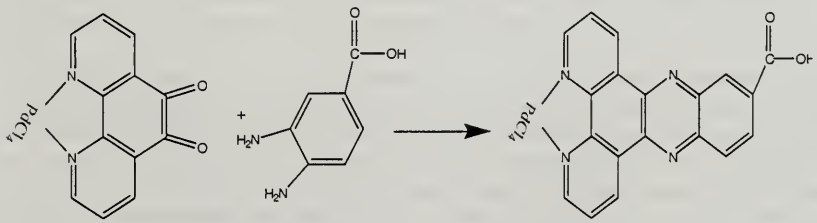
Previous synthesis showed that equimolar amounts of sublimed 3,4-diaminobenzoic acid and dione refluxed for 1 hour in 15 mL of ethanol produced the ethyl-bdppz.[6] This product was also made by refluxing bdppz in 15 mL of ethanol for 1 hour. The product was filtered and an IR and GC/MS were taken (Figure 3 and Figure 4). All glassware was protected from the light with aluminum foil.

Synthesis of glucosified-bdppz (gdppz)



Equimolar amounts of bdppz and glucose were refluxed in 20 mL of 1,1,1-trichloroethane for 2 hours. A pink solution formed and a pinkish precipitate was found after filtration. An IR was taken of the product (Figure 5). All glassware was protected from the light with aluminum foil.

Synthesis of Pd-(bdppz)Cl$_4$



[6] Kinyon, Lindsay. Summer Research **2000.** Dr. Robert Granger Supervisor.

Pd(dione)Cl_4 was synthesized following procedure established by Dr. Robert Granger.[7] Equimolar amounts of Pd(dione)Cl_4 and sublimed 3,4-diaminobenzoic acid were refluxed for three hours in 20 mL of 1,1,1-trichloroethane. The 1,1,1-trichlorethane was rotovapped off and the precipitate was rinsed with distilled H_2O and filtered. An IR was taken of the brownish product (Figure 6). Pd(bdppz)Cl_4 was also synthesized by dissolving equimolar amounts each of Pd(dione) and impure 3,4-diaminobenzoic acid in acetonitrile. The impure 3,4-diaminobenzoic acid was added drop-wise to the hot Pd(dione)/acetonitrile solution. The reaction then was allowed to reflux for 20 to 30 minutes after all of the 3,4-diaminobenzoic acid had been added. A tan precipitate formed and was filtered and dried. An IR was taken of the product (Figure 7). The filtrate was yellow in color and was put on a watch glass so that the solvent could evaporate. An IR was taken of the filtrate product (Figure 8). All glassware and solutions were dried to create an anhydrous environment. Also all glassware was protected from the light with aluminum foil.

Purification of 3,4-diaminobenzoic acid

3,4-diaminobenzoic acid was sublimed using a cold finger sublimation device and vacuum. Two products formed after sublimation. One product was white, orange crystals while the other was a black tar-like compound on the bottom of the sublimation device. These two products were dissolved in HPLC grade methanol. GC/MS chromatogram was obtained and integrated for these products (Figure 9,10). Some impure 3,4-diaminobenzoic acid was also dissolved in HPLC grade methanol and a GC/MS was taken and integrated (Figure 11). The caffeine method was used for all GC/MS analysis. An IR was taken of the sublimed white crystal product. (Figure 12)

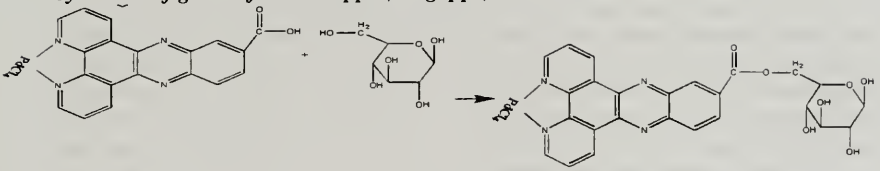
Attempts were made to re-crystallize the impure 3,4-diaminobenzoic acid. Ultra pure water was brought to a boil in a test tube and then saturated with the impure 3,4-diaminobenzoic acid. The test tube was then placed in a beaker of ice and put in the freezer until a precipitate began to fall out. The precipitate was a light brown color. The precipitate was dried and then an IR was taken. (Figure 13). 3,4-diaminobenzoic acid was also dissolved in acetone until saturated. An attempt to re-crystallize the acid was conducted by adding ether to the acetone solution and putting the solution into the refrigerator. A small amount of precipitate formed and it was a yellow, brown color. The precipitate was dried and an IR was taken. (Figure 14).

Solid Phase Extraction was then conducted to try to purify the 3,4-diaminobenzoic acid. The Sep Pak cartridge was prepped and a reverse phase extraction was performed. The 3,4-diaminobenzoic acid was dissolved in ultra pure water and was10mL was loaded onto the cartridge. 5mL of ether was pushed through the cartridge to get rid of as much water as possible. Then 10mL of HPLC grade acetonitrile was pushed through the cartridge. The 3,4-diaminobenzoic acid, acetonitrile solution was collected every 5mL. The first 5mL collected was the only sample that had any color so a GC/MS analysis was taken of this sample (Figure 15).

---

[7] IBID.

Synthesis of glucosified-Pdbdppz (Pd-gdppz)



Pd-bdppz synthesized using the drop-wise addition of impure 3,4-diaminobenzoic acid was sonicated in 20mL of THF until in solution. This solution was then heated and an equimolar amount of glucose and 30 mL of acetonitrile were added to the solution. The resulting solution was allowed to boil for a couple of hours. A tan precipitate formed and was filtered and dried. An IR was taken of this product (Figure 16), and HPLC data was collected by Courtney Arnott on this product (Figures 17, 18, 19)[8]

Conclusions:

Figure 1 shows a very strong peak at 1711 wavenumbers, which is in the correct range for a carboxylic acid peak, 1680 to 1720 wavenumbers. This peak would be expected to show because of the carboxylic acid on the 3,4-diaminobenzoic acid. Figure 2 shows the integrated peaks of the GC/MS of bdppz. The peaks at 207 g/mol, 281 g/mol, and 327 g/mol correlate and match with the compounds that would arise from the breakdown of bdppz.

Figure 3 and Figure 4 prove that esters can be made when a functional group, the carboxylic acid group, is present at the end of the ligand. The IR in Figure 3 has a peak at 1708 wavenumbers, which confirms that the ethyl ester of bdppz was made using the new method because ester peaks appear from 1650 to 1770 wavenumbers. The GC/MS spectrum also supports this synthesis. The peaks at 355 g/mol, 281 g/mol, 207 g/mol, and 73g/mol correlate with compounds that would arise from the breakdown of ethyl-bdppz.

Figure 5(bottom spectrum) has a peak at 1713 wavenumbers in the ester range once again illustrating that the glucose was attached to create an ester on the bdppz, gdppz. When compared to an IR of glucose (top IR spectrum in Figure 5), similar peaks appear in each spectrum supporting this synthesis.

Figure 6 shows the IR spectrum of Pd-bdppz synthesized in 1,1,1-trichloroethane (bottom spectrum) compared to the middle spectrum, 3,4-diaminobenzoic acid, and the top spectrum Pd-dione. The IR spectrum of Pd-bdppz has a peak at 1701 wavenumbers, which falls in the range for carboxylic acid peak. Also similar peaks are found in the Pd-dione and 3,4-diaminobenzoic acid IR spectra. This data supports the synthesis of Pd-bdppz.

[8] Arnott, Courtney. Junior Honors Research. Spring 2002.

Figure 7 shows the IR spectrum of Pd-bdppz synthesized by the drop-wise addition of 3,4-diaminobenzoic acid. This spectrum is the bottom spectrum while the middle spectrum is of Pd-dione, and the top spectrum is of 3,4-diaminobenzoic acid. The IR spectrum of Pd-bdppz has a peak at 1701 wavenumbers, which falls in the range for the carboxylic acid peak. This peak is also at the same wavenumber as the peak in the IR spectrum of Pd-bdppz in Figure 6. This correlation proves that the same product was made using two different methods and also illustrates that the amines on the 3,4-diaminobenzoic acid are more reactive than the carboxylic acid group. Also, similar peaks are found in the Pd-dione spectrum and 3,4-diaminobenzoic acid spectrum that are found in the Pd-bdppz spectrum. This data further supports the synthesis of Pd-bdppz. Figure 8 is the IR spectrum of the filtrate product from the synthesis of Pd-bdppz using the drop-wise addition of 3,4-diaminobenzoic acid. This spectrum has a peak at 1717 wavenumbers, which falls in the carboxylic acid peak range. Because the peak is 16 wavenumbers apart from the carboxylic acid peak found in Figure 6 and Figure 7 of Pd-bdppz, it appears that the filtrate product is a different product. This indicates that maybe the reaction needs to be refluxed longer or two different products are formed from this synthesis reaction. It appears though that the Pd-bdppz precipitates out of solution while the filtrate product does not.

Figures 9, 10 and 11 are the GC/MS results of the sublimed products and impure 3,4-diaminobenzoic acid. Figure 9's chromatogram only has one peak at about 15 to 16 minutes. When determined the molecular weight of this peak is 108 g/mol. Figure 10's chromatogram has two peaks. The first peak is very sharp and at 15 to 16 minutes while the second peak is much broader and first occurs at about 29 minutes. When these peaks are analyzed it appears that the molecular weight of the first one is 108 g/mol and the second is 152 g/mol. Figure 11 has the same two peaks as Figure 10. The peaks in Figure 3 are the same as those in Figure 2. The molecule, 3,4-diaminobenzoic acid, has a molecular weight of 152 g/mol. This data illustrates that the white, sublimed product usually used in synthesis reactions is not the 3,4-diaminobenzoic acid, but the impurity in the product. Both the impure sample and the black tar-like product have peaks for 3,4-diaminobenzoic acid. Figure 12 supports these findings. There is no carboxylic acid peak present in the IR of the sublimed white product. If 3,4-diaminobenzoic acid was present then this peak would appear around 1680 to 1720 wavenumbers because of the carboxylic acid functional group. Since there is no peak, then the carboxylic acid group is lost during sublimation. Maybe during sublimation, the 3,4-diaminobenzoic acid cyclocondenses with itself.

Figure 13 is an IR spectrum of the re-crystallized 3,4-diaminobenzoic acid using ultra pure water. This spectrum reveals that there is no carboxylic acid peak, which would be expected if the product was 3,4-diaminobenzoic acid. Figure 14 is an IR spectrum of the re-crystallized 3,4-diaminobenzoic acid using acetone and ether. This spectrum also reveals that the product is not 3,4-diaminobenzoic acid because no peak around 1680 to 1720 is present. Obviously these attempts to purify 3,4-diaminobenzoic acid using re-crystallization failed, and the carboxylic acid functional group was once again somehow lost.

Figure 15 is a GC chromatogram and mass spectrum of the product obtained using solid phase extraction. The integration does not have significant peaks at 152 g/mol or 108 g/mol. It appears though that peak one might correlate with the impurity while peak two correlates with 3,4-diaminobenzoic acid. Further exploration into these assumptions could be conducted. From the data collected in this experiment, though, it is apparent that the impure 3,4-diaminobenzoic acid needs to be used in the synthesis reactions.

This data though does not correlate with the information obtained from Figures 1 through 6. Figures 1-6 support the fact that sublimed 3,4-diaminobenzoic acid does contain a carboxylic acid group that can form esters. Possibly the sublimed 3,4-diaminobenzoic acid used for these purification experiments was sublimed at too high of temperatures, which might explain why the carboxylic acid group is not present. The appearance of the same peak in Figures 6 and 7 though illustrates that using both sublimed 3,4-diaminobenzoic acid and impure 3,4-diaminobenzoic acid appears to produce the same product.

Figure 16 is the IR spectrum for Pd-gdppz (the bottom spectrum). A peak is present at 1728 wavenumbers, which falls in the ester range. This peak is also at a different wavenumber then any of the other products further supporting the synthesis of a new molecule. The spectra for glucose (middle spectrum) and Pd-bdppz using the drop-wise addition of 3,4-diaminobenzoic acid (top spectrum) are also represented in this figure. Peaks present in the Pd-gdppz spectrum correlate with peaks found in the glucose and Pd-bdppz spectra. This similarity also supports the synthesis of Pd-gdppz.

Figure 17 is the HPLC spectrum for Pd-bdppz. Analysis by Courtney Arnott reveals that the peak for this product appears at a retention time of 6.91 minutes. Figure 18 is the HPLC spectrum for glucose. The peak for glucose appears at 14.03 minutes. Figure 19 is the HPLC spectrum and for Pd-gdppz. Through analysis by Courtney Arnott, the peak for this compound appears at 11.65 minutes. Comparing Figure 19 to Figures 17 and 18 the data reveals that no glucose nor Pd-bdppz is present in the Pd-gdppz compound because peaks at these times do not appear in Figure 19's spectrum. This information implies that a new product was formed and that glucose was attached in some manner to Pd-bdppz. Also the $\lambda_{(max)}$ for glucose was 276 nm, for Pd-bdppz was 280 nm, and for Pd-gdppz was 224 nm. The significant difference between the $\lambda_{(max)}$ for Pd-gdppz and the other compounds further supports the synthesis of a new product.

Further Experimentation:

The above conclusions support the synthesis of the bdppz ligand and Pd-bdppz. The data also supports the synthesis of gdppz, Pd-gdppz and other esters of the bdppz ligand. Further experimentation needs to be conducted for characterization of these products using NMR, HPLC, and crystal structures.

The synthesis of Pd-gdppz could probably be conducted solely in acetonitrile without the addition of THF, because both the Pd-bdppz and glucose appear to be soluble in acetonitrile. Experiments need to be conducted to prove this hypothesis.

NMR data needs to be conducted on the Pd-bdppz products from both methods of synthesis, and the Pd-gdppz product.

Crystal growth chambers need to be established for the Pd-bdppz and gdppz products.

Other attempts have been made to attach glucose to Pd-bdppz. These attempts need to be further investigated. Different products were obtained. Characterization and analysis of these products need to be done using FT/IR, HPLC and NMR.

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ABSTRACT

Payne, Emma Kate. B.S., Sweet Briar College, May 2003. The Synthesis and Characterization of Novel Platinum and Palladium Diimene Compounds for Use as Anticancer Drugs and CO_2 Reduction Catalysts. Research Advisor: Dr. Robert Granger.

Current research at Sweet Briar College is focused on the synthesis, purification, and characterization of novel platinum and palladium diimene compounds for use as anticancer drugs and CO_2 reduction catalysts. Novel synthetic schemes were developed for the ligands, dipyridophenazine benzoic acid, ethyl-dipyridophenazine, and glucosified-dipyridophenazine. The dipyridophenazine benzoic acid and ethyl-dipyridophenazine ligands were characterized using IR spectroscopy and GC/MS. The glucosified-dipyridophenazine was characterized using IR spectroscopy. Further characterization of these ligands was inhibited due to their low solubility in common solvents. [Pt(1,10-phenanthroline-5,6-dione)Cl_4] was characterized using IR spectroscopy, NMR spectroscopy, X-ray crystallography, and a cyclic voltamogram. Novel synthetic schemes were developed for [Pt(dipyridophenazine benzoic acid)Cl_4], [Pd(dipyridophenazine benzoic acid)Cl_4], [Pd(glucosified-dipyridophenazine benzoic acid)Cl_4]. These metal complexes were characterized using IR spectroscopy, but solubility problems hindered further characterization. A novel synthetic scheme was also developed for [Pt(1,10-phenanthroline-5,6-dione)$_2$(Tartrate)]. This metal complex was characterized using IR spectroscopy and NMR spectroscopy. A novel synthetic scheme was developed for the CO_2 reduction catalyst [Pd(di-2-pyridolketone)$_2$(PF_6)]$_n$. This polymer was characterized using IR spectroscopy and X-ray crystallography.

The Synthesis and Characterization of Novel Platinum and Palladium Diimene Compounds for Use as Anticancer Drugs and CO_2 Reduction Catalysts

Section 1: Project Significance and Background on Developed Compounds

Section 1.1: Introduction

This thesis focuses on the development, synthesis, purification, and characterization of platinum and palladium 2+ and 4+ transition metal diimene compounds. The synthesis and characterization of different diimene ligands was also investigated. The compounds discussed throughout this thesis showed powerful evidence for use as anticancer drugs and CO_2 reduction catalyst.

Section 1.2: Background on the Platinum and Palladium Diimene Compounds Synthesized

Transition metals usually have more than one stable oxidation state. Multiple oxidation states result from the loss of electrons from the transition metal's d-orbitals.[1] Platinum and palladium have two common oxidation states, 2+ and 4+.

The number of atoms bound to the metal center is known as the coordination number of the complex[1]. Platinum and palladium commonly form complexes with coordination numbers of four and six. The platinum and palladium (2+) centers form complexes with a coordination number of four. These compounds have square planar molecular geometries (Figure 1.1). The figure below illustrates the square planar molecule, where M represents the transition metal center and L represents a ligand.

Figure 1.1: Representation of a Square Planar Transition Metal Complex

The platinum and palladium (4+) form complexes with a coordination number of six.[1] These compounds have octahedral molecular shapes (Figure 1.2). The figure below illustrates the octahedral molecule, where M represents the transition metal center and L represents a ligand.

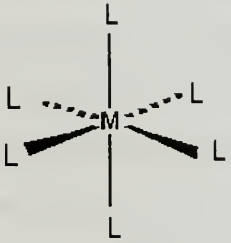
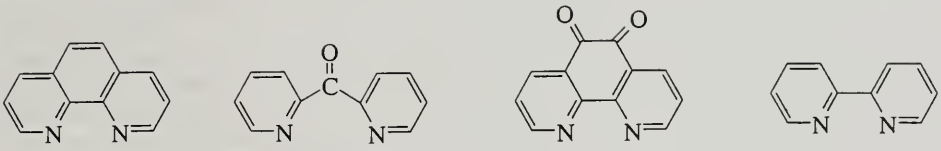


Figure 1.2: Representation of an Octahedral Transition Metal Complex

During this project small organic molecules called ligands were bound to the metal center.[1] The types of ligands used were bidentate ligands. Bidentate ligands can simultaneously occupy two sites on the metal center. The bidentate ligands were diimene compounds, or a compound containing an sp^2-hybridized nitrogen (Figure 1.3).



1,10-phenanthroline (phen) | di(2-pyridyl) ketone (DPK) | 1,10-phenanthroline-5,6-dione (dione) | 2,2'-dipyridine (dipy)

Figure 1.3: Examples of Bidentate Ligands

Section 2: Instrumental and Materials

Section 2.1: Instrumental

All infrared spectra were obtained on a 4020 Galaxy Series Fourier Transform-Infrared (FT/IR) as KBr pellets. A 5890 Series II Plus Gas Chromatograph and a Hewlett-Packard Mass Spectrometer and software were used to obtain gas chromatograms and mass spectra. All Nuclear Magnetic Resonance (NMR) spectra were obtained on an EX 400 MHz JEOL and all chemical shifts were measured in ppm. All x-ray structures were obtained by Peter White at the University of North Carolina, Chapel Hill. The High Resolution Mass Spectrometer spectra were taken by Don Dick at Colorado State. Cyclic Voltammetry was conducted by Nicole Crowder on an EG&G Princeton Applied Research Model 263A using a standard three electrode set-up.

Section 2.2: Materials

3,4-diaminobenzoic acid- Aldrich
1,1,1-trichloroethane- VWR, Aldrich
Ethanol-VWR
Glucose- Aldrich
Acetonitrile- Aldrich
Nitrogen- BOC Gases
Dimethylformamide- Aldrich
Potassium hexachloroplatinate(IV)- Aldrich
Dimethylsulfoxide- Aldrich
Ether- VWR
Potassium hexachloropalladate(IV)- Aldrich

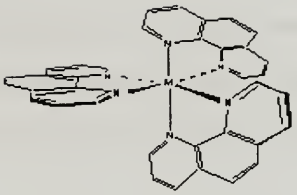
Potassium bromide- Baker
Nitric acid- VWR
Hydrochloric acid- VWR
Sodium hydroxide- Baker
Molecular sieves- Aldrich
Tetrahydrofuran- VWR, Baker
Glucosamine hydrochloride- Aldrich
Potassium tetrachloropalladate(II)- Aldrich
Methanol- VWR
Silver Nitrate- Baker
Tartaric acid- Baker
Palladium (II) chloride- Aldrich
Nitrobenzene- Aldrich
Potassium hexaflorophosphate- Aldrich
Celite- Aldrich
Sodium tetraphenylborate- Aldrich
Potassium tetrachloraplatinate(II)- Aldrich
Deuterium oxide- Aldrich
1,10-phenanthroline- Aldrich
Di(2-pyridyl)ketone- Aldrich
Acetone-VWR
Sulfuric Acid-VWR
Lithium perchlorate- Baker

Section 3: Metal Based Anticancer Drugs: Background, Synthesis, Results and Conclusions

Section 3.1: Metal Based Anticancer Drugs: Background

Beginning in the early 1980s, researchers began examining the interactions of transition metals copper, nickel, zinc, iron, cobalt, chromium, rhodium, osmium, and ruthenium diimene complexes with DNA.[2] Many of these compounds have demonstrated site-specific DNA interactions. Diimene compounds containing platinum and palladium were absent from these studies.

In the summer of 1996, Dr. Robert Granger developed a new scheme for the synthesis of water-soluble platinum 4+ diimene complexes.[3] He was able to characterize the complex $[Pt(phen)_3][PF_6]_4$ (Figure 3.1).[3]



[M(phen) $_3$]$^{4+}$; M = Pt & Pd

Figure 3.1: $[Pt(phen)_3][PF_6]_4$

This complex was found to interact with DNA in a similar manner as the previously studied octahedral transition metal diimene complexes.

Today most chemotherapeutic agents that contain a metal center are platinum metal based anticancer drugs. One such agent is cisplatin. Cisplatin (Figure 3.2) was synthesized in 1844 by Michelle Peyrone[4], but it was not until 1965, that Barnett Rosenberg observed the anticancer properties of platinum complexes.

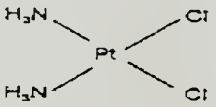


Figure 3.2: Structure of Cisplatin
Figure Taken From Lippard, 1999.

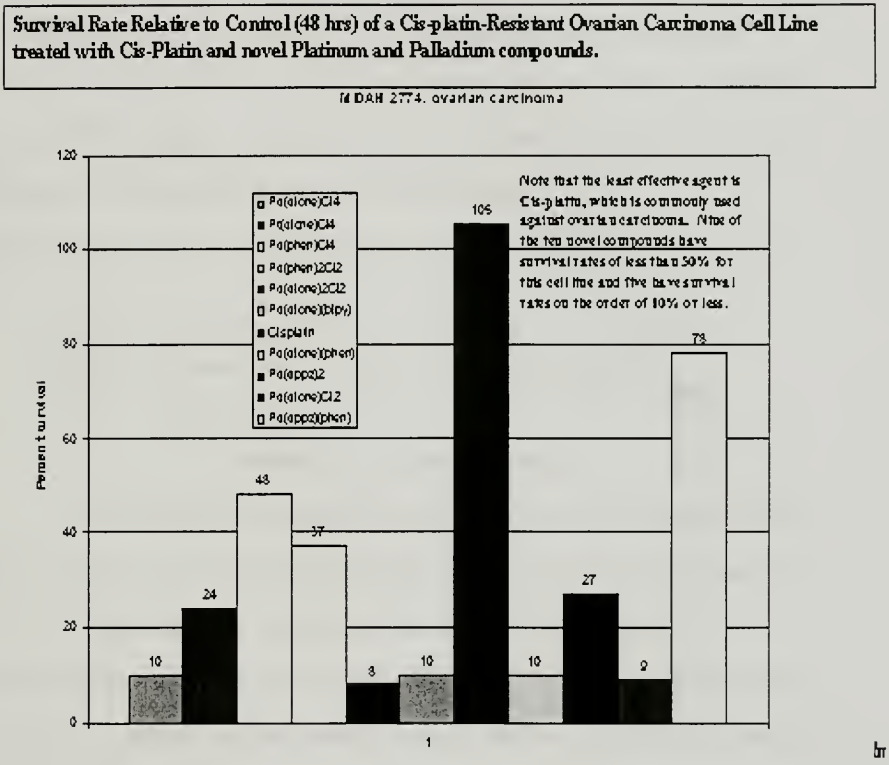
Cisplatin became the first platinum compound to be approved for cancer therapy and was first administered to a cancer patient in 1971.[4] Today cisplatin is the most widely used cytotoxic agent.

Cisplatin is used with testicular, bladder, germ cell, head, neck, small cell lung, and ovarian cancers. A shortcoming of cisplatin though is the fact that many cancers

develop resistance to the drug. Resistance occurs when the drugs no longer affect certain mechanisms in the cells. In addition to developing resistance to the drug, cisplatin also places a good deal of stress on the organs, bone marrow, and nervous system. Despite these negative effects, cisplatin is still the most widely used platinum based anticancer drug.[4]

Because many chemotherapeutic metal based agents contain platinum, and because cells develop resistance to cisplatin, Dr. Granger wanted to test the bioactivity of his platinum and palladium 4+ complexes against malignant cells. In 1997 Dr. Robin Davies began preliminary cell culture using Dr. Granger's novel compounds. Many of the compounds showed bioactivity towards the cancerous cell lines. The graph (Figure 3.3)[5] below illustrates the survival rate of a cisplatin resistant cell line after treatment with different novel platinum and palladium diimene compounds. All the novel compounds proved to be more effective than cisplatin.

Figure 3.3: Graph of the Survival Rate Of a Cisplatin Resistant Ovarian Carcinoma Cell Line Treated with Cisplatin and Novel Platinum and Palladium Compounds

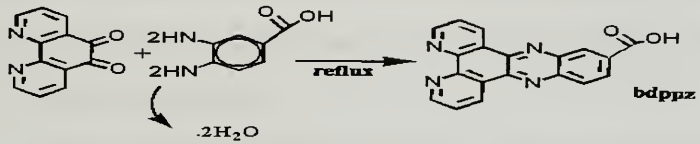


The anticancer compound-synthesis research conducted throughout this thesis focuses on two different aspects. One focus is to characterize some of the novel compounds that have been previously tested. The other focus is to synthesize more novel platinum and palladium diimene compounds to enhance the cytotoxicity and selectivity of the compounds.

Enhancing the selectivity of the compounds stems from the fact that cancer cells have a much higher metabolism than normal cells. To accommodate this faster metabolism, cancer cells have adapted mechanisms to actively transport nutrients into the cell. In theory an anticancer drug with a nutrient attached, like glucose, would be taken up by the cancer cells more rapidly than by the normal cells. This uptake hopefully would result in an increased mortality rate for cancer cells and a decrease in available drug for the healthy cells. The drug would be more selective in targeting cancer cells.[6]

Section 3.2: Metal Based Anticancer Drugs: Synthesis

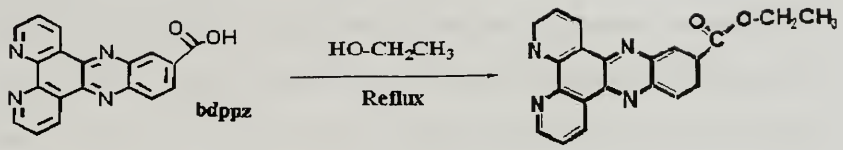
Section 3.2.1: Synthesis of dipyridophenazine benzoic acid (bdppz) (Scheme 3.2.1)



Scheme 3.2.1: Synthesis of bdppz

In a 50 mL round bottom flask, 0.0075 g of sublimed 3,4-diaminobenzoic acid and 0.01045 g of 1,10-phenanthroline-5,6-dione (dione) were refluxed for 2 hours in 15 mL of 1,1,1-trichloroethane. A light brown precipitate formed. The 1,1,1-trichloroethane was removed using a rotary evaporator. The remaining solution was run through a sintered glass Buchner funnel (frit) and put on the vacuum manifold (vac-line) to dry. The synthesis of dione followed that established by Eisenberg.[7] Using a cold finger, the 3,4-diaminobenzoic acid was sublimed to dispose of impurities. White, orange crystals formed on the cold finger and were used in the reaction. All glassware containing the bdppz was wrapped in aluminum foil because we suspect that the compound is sensitive to light. An FT/IR (Figure A1, Appendix A) and mass spectrum (Figure B1, Appendix B) were taken of the product.

Section 3.2.2: Synthesis of ethyl-bdppz (Scheme 3.2.2)

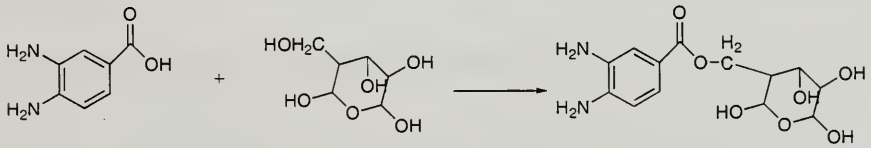


Scheme 3.2.2: Synthesis of ethyl-bdppz

Section 3.2.2A: This synthesis was conducted by a previous student, Lindsay Kenyon.[8] In a round bottom flask, 0.0052 g of sublimed 3,4-diaminobenzoic acid and 0.007253 g dione were refluxed for 1 hour in 15 mL of ethanol. A pale yellow precipitate formed and was filtered on a frit and put on the vac-line to dry. An FT/IR (Figure A2, Appendix A) and a mass spectrum were taken of the molecule. These spectra were used for comparisons.

Section 3.2.2B: This product was also made by refluxing 0.0135 g of bdppz in ethanol for 1 hour. While the solution was still hot, it was poured into a beaker that was on ice. A pale, yellow precipitate formed. The precipitate was collected on a frit and placed on the vac-line to dry. All glassware was wrapped in aluminum foil because we suspect the compound to be sensitive to light. An FT/IR (Figure A3, Appendix A) and mass spectrum (Figure B2, Appendix B) were taken of this product.

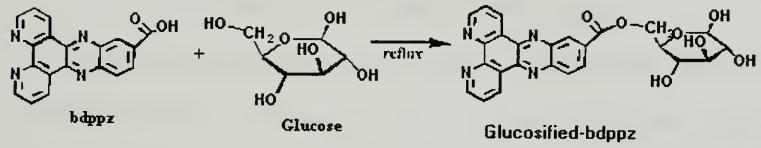
Section 3.2.3: Synthesis of 3,4-diaminobenzoic acid- glucose (Scheme 3.2.3)



Scheme 3.2.3: Synthesis of 3,4-diaminobenzoic acid-glucose

Into 50 mL of acetonitrile, 0.1033 g of 3,4-diaminobenzoic acid. In another 50 mL of acetonitrile, 0.1223 g of glucose was dissolved. All glassware was dried and purged with N_2. Using an addition funnel, the glucose solution was added dropwise to the 3,4-diaminobenzoic acid solution. A light brown precipitate formed and an FT/IR (Figure A4, Appendix A) of the compound was taken.

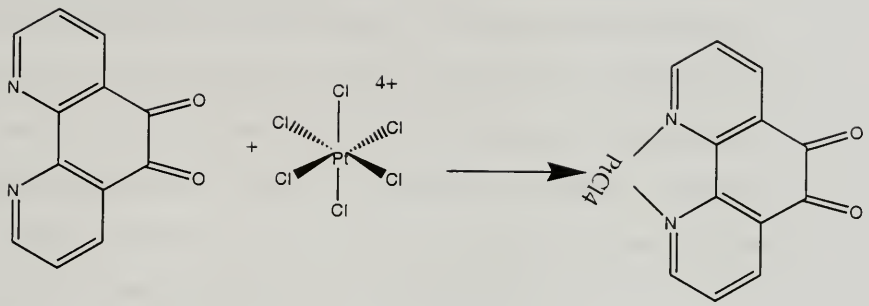
Section 3.2.4: Synthesis of glucosified- bdppz (gbdppz) (Scheme 3.2.4)



Scheme 3.2.4: Synthesis of gbdppz

For 5 hours, 0.0948 g of bdppz and 0.05346 g of glucose were refluxed in 20 mL of 1,1,1-trichloroethane. The solution turned a peachy, pink color and contained a pink precipitate. The solvent from the 1,1,1-trichloroethane solution was allowed to evaporate overnight, while the pink precipitate was collected on a frit and dried on the vac-line. All glassware was covered in aluminum foil because we believe the compound to be sensitive to light. An FT/IR (Figure A5, Appendix A) was taken of the pink precipitate. (This reaction was also attempted in DMF, but the DMF attached to the bdppz instead of the glucose.)

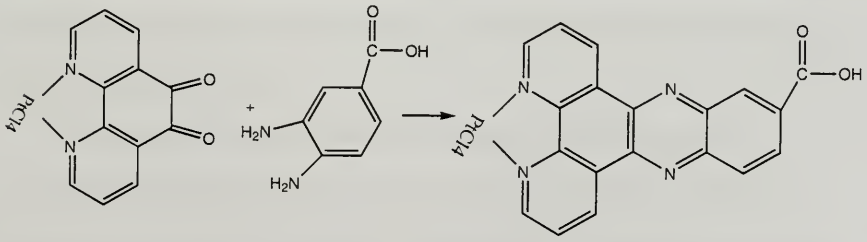
Section 3.2.5: Synthesis of [Pt(dione)Cl_4] (Scheme 3.2.5)



Scheme 3.2.5: Synthesis of [Pt(dione)Cl_4]

In 15 mL of ultra pure water, 0.100 g of K_2PtCl_6 was dissolved. Also in 15 mL of ultra pure water, 0.040 g of dione was dissolved. The two solutions were combined and left stirring for 48 hours. A yellow, orange precipitate formed. The precipitate was collected on a frit and left to dry on the vac-line. An FT/IR spectrum (Figure A6, Appendix A) and NMR spectra (Figures C1-C3, Appendix C) were taken of the product. A crystal suitable for analysis was obtained through slow diffusion of DMSO and ether (Figures D1-D30, Appendix D).

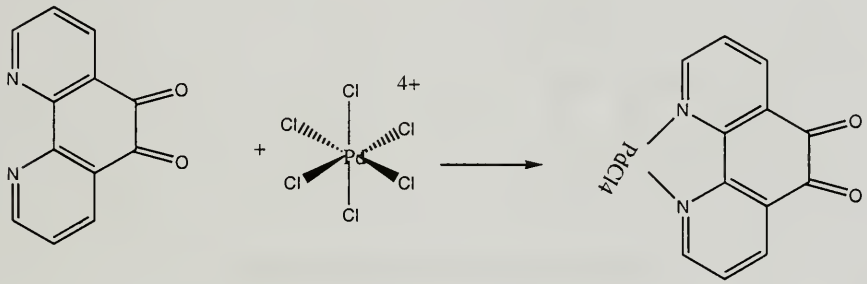
Section 3.2.6: Synthesis of [Pt(bdppz)Cl_4] (Scheme 3.2.6)



Scheme 3.2.6: Synthesis of [Pt(bdppz)Cl_4]

For 1 hour, 0.0100 g of [Pt(dione)Cl_4] and 0.00319 g of 3,4-diaminobenzoic acid were refluxed in 15 mL of 1,1,1-trichloroethane. An olive green precipitate formed indicating that some of the metal had been reduced because usually a reduced metal has a gray, black color. The 1,1,1-trichloroethane was removed using a rotary evaporator and an FT/IR spectrum(Figure A7, Appendix A) was taken of the precipitate. All glassware was wrapped in aluminum foil because we believe the compound to be sensitive to light.

Section 3.2.7: Synthesis of [Pd(dione)Cl_4] (Scheme 3.2.7)



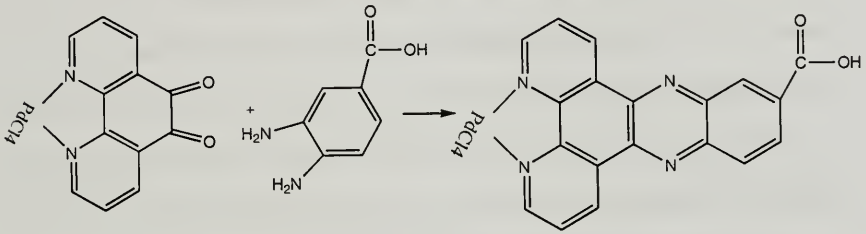
Scheme 3.2.7: Synthesis of [Pd(dione)Cl_4]

Section 3.2.7A: Equimolar amounts of K_2PdCl_6 and dione were dissolved separately in 15 mL of ultra pure water. These solutions were combined and allowed to stir for 72 hours until an orange, yellow precipitate formed. The precipitate was collected on a frit and allowed to dry on the vac-line. An FT/IR spectrum (Figure A8, Appendix A) was taken of the product.

Section 3.2.7B: In order to make a purer product, an effort to make [Pd(dione)Cl_4] from [Pd(phen)Cl_4] was tried. For 72 hours 0.2076g of K_2PdCl_6 and 0.4708g of 1,10-phenanthroline were left stirring in 50 mL of distilled water. A light yellow precipitate formed. The product was collected on a frit and placed on the vac-line to dry. An FT/IR spectrum (Figure A9, Appendix A) was taken of the product. Then

1.00 g of the $[Pd(phen)Cl_4]$ and 0.2796 g of KBr were refluxed for three hours in 5 mL of concentrated HNO_3 (aq) and 10mL of concentrated HCl (aq). After refluxing, the pH of the solution was lowered to 5.3 using 10 M NaOH. A pale yellow product formed and was collected on a frit and put on the vac-line to dry. An FT/IR spectrum was taken of the product (Figure A9).

Section 3.2.8: Synthesis of $[Pd(bdppz)Cl_4]$ (Scheme 3.2.8)

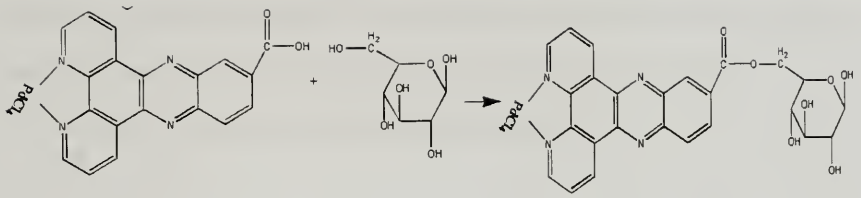


Scheme 3.2.8: Synthesis of $[Pd(bdppz)Cl_4]$

Into 15-20 mL of acetonitrile, 0.0511 g of $[Pd(dione)Cl_4]$ was dissolved. Into 15 to 20 mL of acetonitrile, 0.01696 g of 3,4-diaminobenzoic acid was also dissolved. The 3,4-diaminobenzoic acid solution was added dropwise to the warm dione solution. Once all the 3,4-diaminobenzoic acid was added, the solution was allowed to reflux for 30 minutes. A tan precipitate was collected on a frit and put on the vac-line to dry. All glassware was covered with aluminum foil because we believe the bdppz ligand to be sensitive to light. An FT/IR spectrum (Figure A10, Appendix A) was taken of the tan precipitate collected.

(This synthesis was first attempted in 1,1,1-trichloroethane, but no reaction occurred).

Section 3.2.9: Synthesis of $[Pd(gbdppz)Cl_4]$ (Scheme 3.2.9)

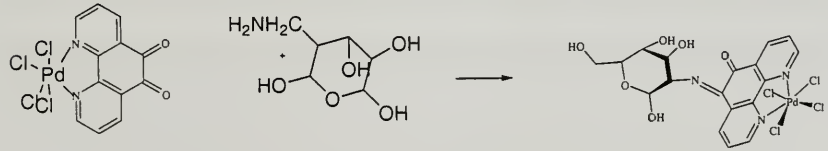


Scheme 3.2.9: Synthesis of [Pd(gbdppz)Cl_4]

In a round bottom flask, 0.0118 g of [Pd(bdppz)Cl_4] and 0.004875 g of glucose were put in 20-30 mL of acetonitrile that had been dried over molecular sieves. The solution refluxed for about 1 hour and a tan precipitate formed. The precipitate was collected on a frit and dried on the vac-line. All glassware was wrapped with aluminum foil because we believe this compound to be sensitive to light. An FT/IR spectrum (Figure A11, Appendix A) was taken.

(This reaction was first attempted in THF, but was unsuccessful because it did not yield the desired product.)

Section 3.2.10: Synthesis of [Pd(dione-glucosamine)Cl_4] (Scheme 3.2.10)

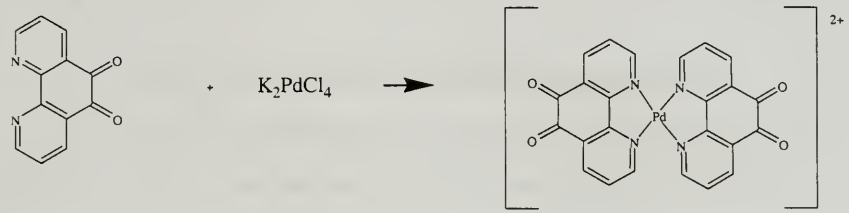


Scheme 3.2.10: Synthesis of [Pd(dione-glucosamine)Cl_4]

A 1:2 molar ratio of [Pd(dione)Cl_4] to glucosamine was dissolved separately in 10 to 15 mL of acetonitrile each and left to stir over night. The glucosamine solution was then added to the metal solution and refluxed for 1 hour. A pale yellow precipitate

formed and was filtered, collected on a frit, and dried under vacuum. An FT/IR spectrum (Figure A12, Appendix A), High Resolution Mass Spectra (Figures E1-E4, Appendix E), and NMR spectra (Figures C4-C5, Appendix C) were taken of the precipitate.

Section 3.2.11: Synthesis of $[Pd(dione)_2]Cl_2$ (Scheme 3.2.11)

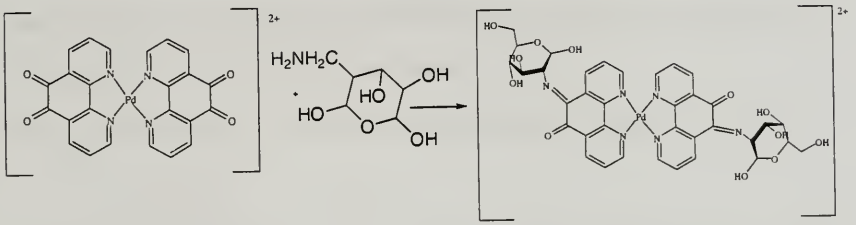


Scheme 3.2.11: Synthesis of $[Pd(dione)_2]Cl_2$

A 2:1 molar ratio of dione to K_2PdCl_4 was dissolved separately in about 10 mL of methanol each. The dione solution was then added to the metal solution and a yellow precipitate began to form. The solution was refluxed for 1 hour and the yellow precipitate was filtered, collected on a frit, and dried under vacuum. An FT/IR spectrum (Figure A13, Appendix A), High Resolution Mass Spectra (Figures E5-E8), and NMR spectrum (Figure C6, Appendix C) were taken of the product.

(Other attempts were first made to create this molecule. Ag_2Tartrate was used to strip $PdCl_4$ of the chlorines and then attach the dione. Different ratios of methanol and water solutions were also used when trying to synthesize using K_2PdCl_4. None of these were successful.)

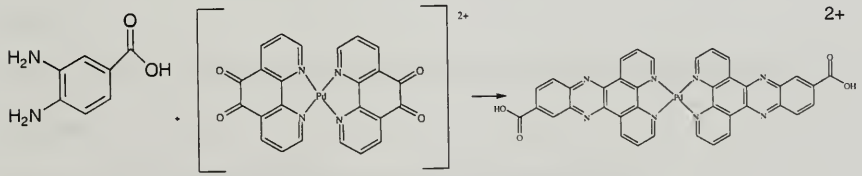
Section 3.2.12: Synthesis of $[Pd(dione\text{-}glucosamine)_2]Cl_2$ (Scheme 3.2.12)



Scheme 3.2.12: Synthesis of $[Pd(dione\text{-}glucosamine)_2]Cl_2$

A 1:2 molar ratio of $[Pd(dione)_2]Cl_2$ to glucosamine was dissolved separately in about 10 to 15 mL of acetonitrile each and left to stir over night. The glucosamine solution was then added to the metal solution and refluxed for an hour. A pale yellow precipitate formed which was filtered, collected on a frit, and dried under vacuum. An FT/IR spectrum (Figure A14, Appendix A), High Resolution Mass Spectra (Figures E9-E12, Appendix E), and NMR spectra (Figures C7-C8, Appendix C) were taken of the precipitate.

Section 3.2.13: Synthesis of $[Pd(bdppz)_2]Cl_2$ (Scheme 3.2.13)

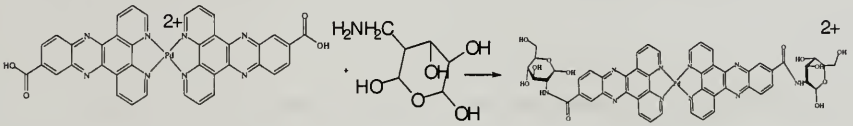


Scheme 3.2.13: Synthesis of $[Pd(bdppz)_2]Cl_2$

A 1:2 molar ratio of $[Pd(dione)2]Cl_2$ to 3,4-diaminobenzoic acid was each dissolved and left to stir over night in 10 to 20 mL of acetonitrile. The 3,4-diaminobenzoic acid was then added to the metal solution and a brownish-yellow precipitate began to form. The solution was refluxed for 1 hour. The brownish-yellow precipitate was collected on a frit and dried under vacuum. All glassware was wrapped in

aluminum foil because we believe the bdppz ligand is sensitive to light. An FT/IR spectrum (Figure A15, Appendix A) and High Resolution Mass Spectra (Figures E13-E16, Appendix E) were taken of the precipitate.

Section 3.2.14: Synthesis of $[Pd(bdppz\text{-}glucosamine)_2]Cl_2$ (Scheme 3.2.14)



Scheme 3.2.14: Synthesis of $[Pd(bdppz\text{-}glucosamine)_2]Cl2$

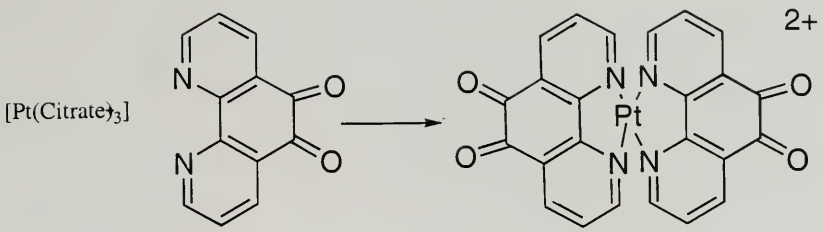
A 1:2 molar ratio of $[Pd(bdppz)_2]Cl_2$ and glucosamine was dissolved in cyclohexane separately and left to stir over night. The glucosamine solution was added to the metal solution and allowed to reflux for about 1 hour. A yellow precipitate formed and was collected on a frit and dried on the vac-line. Once again all glassware was wrapped in aluminum foil because we believe this compound to be sensitive to light. An FT/IR spectrum (Figure A16, Appendix A), NMR spectra (Figures C9-C10, Appendix C), and High Resolution Mass Spectra (Figures E17-E21, Appendix E) were taken of the product.

(This synthesis was first attempted in nitrobenzene, but the desired product was not obtained.)

Section 3.2.15: Synthesis of $[Pt(dione)_2](PF_6)_2$ (Scheme 3.2.15)

Scheme 3.2.15: Synthesis of $[Pt(dione)_2](PF_6)_2$

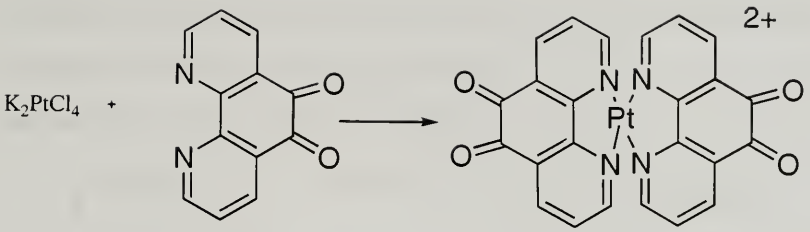
$$K_2PtCl_4 + Ag_3Citrate \longrightarrow [PtCitrate_3]$$



Section 3.2.15A: In about 10-15 mL of ultra pure water, 0.0112 g of K_2PtCl_4 was dissolved. Next 0.0247 g of $Ag_3Citrate$ was added and the solution was allowed to stir for 5 hours. Then the solution was refluxed until the solution turned light brown. The solution was then run through celite® and a pale yellow filtrate was collected. To the filtrate 0.00966 g of dione was added and the solution was left spinning until the dione was dissolved. To the solution, 0.00665 g of KPF_6 was added, and the solution turned gray, brown. No product was obtained.

Section 3.2.15B: This same procedure was followed using equimolar amounts of $Ag_2Tartrate$ instead of $Ag_3Citrate$. After adding the KPF_6 a small amount of a brown precipitate formed. The solution was put on a watch glass and was left in a hood to allow the water to evaporate. An FT/IR spectrum (Figure A17, Appendix A) was taken of the waxy product gathered on the watch glass. The $Ag_2Tartrate$ was made by combining equimolar amounts of $AgNO_3$ and tartaric acid in water. The solution was left stirring until all was dissolved. Then the $Ag_2Tartrate$ was precipitated out using acetone. The white precipitate was collected on a frit and dried on a vac-line.

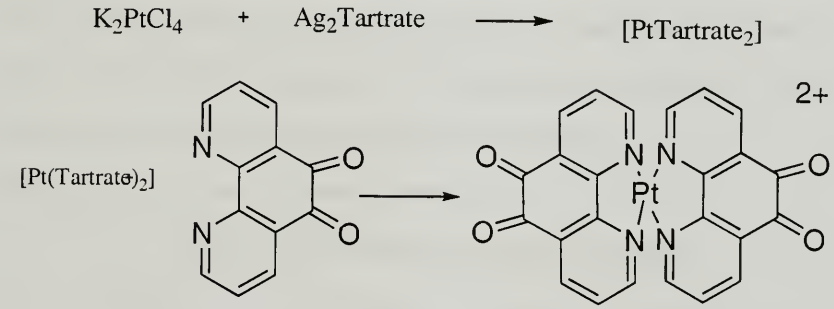
Section 3.2.16: Synthesis of $[Pt(dione)_2]Cl_2$ (Scheme 3.2.16)



Scheme 3.2.16: Synthesis of $[Pt(dione)_2]Cl_2$

For 5 days 0.0200 g of K_2PtCl_4 and 0.0204 g of dione were left stirring in 10 mL of ultra pure water. A yellow precipitate formed. This product was collected on a frit and dried on the vac-line. A FT/IR spectrum (Figure A18, Appendix A) was taken of the precipitate.

Section 3.2.17: Attempted Synthesis of $[Pt(dione)_2](ClO_4)_2$ (Scheme 3.2.17)

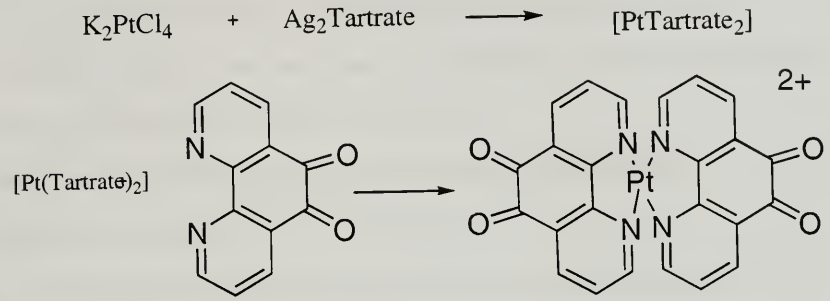


Scheme 3.2.17: Attempted Synthesis of $[Pt(dione)_2](ClO_4)_2$

In 12 mL of ultra pure water 0.0200 g of K_2PtCl_4 was dissolved. To the solution 0.03504 g of Ag_2Tartrate was added, and the solution was allowed to stir for 1 hour. The solution was then refluxed until it turned a light brown color. The solution was then run through celite® and a pale yellow filtrate was obtained. To the filtrate 0.0173 g of dione

was added and allowed to stir until the dione had dissolved. Then 0.0069 g of $LiClO_4$ was added to the solution, but no precipitate formed.

Section 3.2.18: Synthesis of $[Pt(dione)_2](BPh_4)_2$

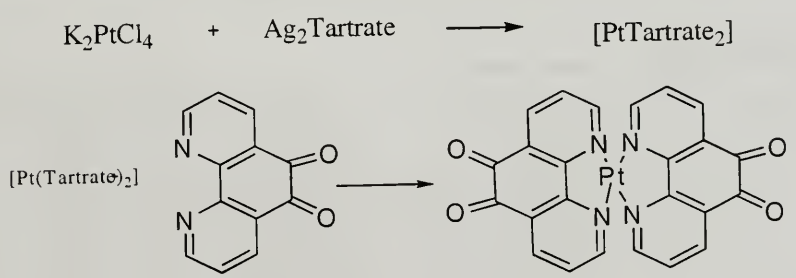


Scheme 3.2.18: Synthesis of $[Pt(dione)_2](BPh_4)_2$

The same quantities and procedure in 3.2.17 were followed. Instead of adding $LiClO_4$, 0.0221 g of $NaBPh_4$ was added to the solution. A reddish brown precipitate formed. This precipitate was collected on a frit and put on the vac-line to dry. On the vac-line the product turned gray and we believe it decomposed.

Section 3.2.19: Synthesis of $[Pt(dione)_2(Tartrate)]$

Scheme 3.2.19: Synthesis of $[Pt(dione)_2(Tartrate)]$



Over night, 0.0200 g K_2PtCl_4 and 0.0351 g of $Ag_2Tartrate$ were left stirring in 15 mL of ultra pure water. The solution was then refluxed for about 1 hour or until it turned

light brown. The solution was run through celite® and a pale yellow filtrate was collected. To the filtrate, 0.0137 g of dione was added. This solution was left stirring until the dione had dissolved. The solution was then placed on a watchglass in a hood so that the water could evaporate. A light brown precipitate was collected off the watchglass. An FT/IR spectrum (Figure A19, Appendix A) and NMR spectra (Figure C11-C13, Appendix C) were taken of the product.

Section 3.3: Metal Based Anticancer Drugs: Results and Conclusions

Section 3.3.1: FT/IR Characterization Background

When using FT/IR Spectra to characterize and compare different molecules, it is important to look for peaks that are characteristic of functional groups. In some molecules I looked for the carboxyl peak that occurs from 1680 to 1720 wavenumbers. In other molecules that I synthesized, I looked for the carbonyl stretch that usually has a peak between 1660-1740 wavenumbers.[9] Table 1 summarizes at what wavenumbers the carboxyl peak and carbonyl peak are found in the metal based anticancer drugs that were synthesized. Also when comparing FT/IR spectra, one looks for similar peak patterns.

Table 1: Summary of the Carbonyl and Carboxylic Acid Stretches Found in the FT/IR Spectra of the Compounds Synthesized

Synthesis Section #	Name of Compound	Wavenumbers of carbonyl Stretch cm^{-1}	Wavenumbers of Carboxylic Acid Stretch cm^{-1}
3.2.1	bdppz		1711.62
3.2.2A	ethyl-bdppz	1708.24	
3.2.2B	ethyl-bdppz	1707.47	
3.2.3	3,4-diaminobenzoic acid-glucose	1680.47	
3.2.4	gbdppz	1712.48	
3.2.5	[Pt(dione)Cl_4]	1701.68	
3.2.6	[Pt(bdppz)Cl_4]		1703.42
3.2.7A	[Pd(dione)Cl_4]	1701.68	
3.2.7B	[Pd(dione)Cl_4]	1722.90	
3.2.8	[Pd(bdppz)Cl_4]		1701.30
3.2.9	[Pd(gbdppz)Cl_4]	1728.30	

3.2.10	[Pd(dione-glucosamine)Cl_4]	1701.68	
3.2.11	[Pd(dione)$_2$]Cl_2	1705.73	
3.2.12	[Pd(dione-glucosamine)$_2$]Cl_2	1699.76	
3.2.13	[Pd(bdppz)$_2$]Cl_2		1727.72
3.2.14	[Pd(bdppz-glucosamine)$_2$]Cl_2	1703.42	
3.2.15B	[Pt(dione)$_2$](PF_6)$_2$	1693.20	
3.2.16	[Pt(dione)$_2$]Cl_2	1702.46	
3.2.19	[Pt(dione)$_2$(Tartrate)]	1693.97	

Section 3.3.2: Results from the synthesis of bdppz

Analysis of the spectra led us to believe that we were successful in synthesizing the bdppz ligand. The FT/IR spectrum (Figure A1) of the bdppz compound shows a very strong peak at 1711.62 wavenumbers, which is in the correct range for a carboxyl peak, 1680 to 1720 wavenumbers. This peak would be expected to show because of the carboxylic acid on the 3,4-diaminobenzoic acid. The mass spectrum of bdppz (Figure B1) shows peaks at 207 g/mol, 281 g/mol, and 327 g/mol. These peaks correlate and match with the compounds that would arise from the breakdown of bdppz.

Section 3.3.3: Results from the synthesis of ethyl-bdppz

Section 3.3.3A This synthesis was previously conducted by another student who was able to collect an FT/IR and GC/MS of the product.[8] I used the previous FT/IR spectrum (Figure A2) as a comparison and the product I made matched the one previously made. In the FT/IR spectrum a carbonyl peak appears at 1708.24 wavenumbers, which falls in the expected range.

Section 3.3.3B This synthesis proves that the ester can be made more than one way. Previously the synthesis of the ethyl-bdppz was conducted by refluxing the 3,4-diaminobenzoic acid and dione in ethanol. In this synthesis the ethyl-ester was made by refluxing the bdppz ligand in ethanol. The FT/IR spectrum (Figure A3) has a peak at 1707.47 wavenumbers, which confirms that the ethyl ester of bdppz was made using the

new method because ester peaks appear from 1660 to 1740 wavenumbers. The carbonyl peak in the FT/IR spectrum of the previous synthesis, A2, and in the FT/IR of this synthesis, A3, are less than one wavenumber apart. This small difference implies that the same molecule has been made. Usually a difference in three to four wavenumbers is necessary to distinguish two molecules different from each other. The mass spectrum (Figure B2) also supports this synthesis. The peaks at 355 g/mol, 281 g/mol, 207 g/mol, and 73g/mol correlate with compounds that would arise from the breakdown of ethyl-bdppz.

Section 3.3.4: Results from the synthesis of 3,4-diaminobenzoic acid-glucose

The FT/IR spectrum (Figure A4) leads us to believe that the 3,4-diaminobenzoic acid-glucose ligand was synthesized. The FT/IR spectrum shows a very strong carbonyl peak at 1680.47 wavenumbers, which follows the expected range of a carbonyl band. The broad band from 2700 to 3000 wavenumbers also supports this synthesis. This broad band is expected of OH groups, which are found on the glucose. Further support is provided when the FT/IR of the 3,4-diaminobenzoic acid-glucose is compared to the FT/IR spectrum of glucose (A23). Peaks at 3000-3500 and 1000 wavenumbers that are characteristic of glucose are present in both spectra.

Section 3.3.5: Results of the synthesis of gbdppz

We have strong spectroscopic data that supports the synthesis of the gbdppz ligand. The FT/IR spectrum of the gbdppz ligand (Figure A5) includes a carbonyl peak in the expected range at 1712.48 wavenumbers. Furthermore, the OH peaks associated with glucose can be seen at 2700 to 3000 wavenumbers. See Figure A23 (Appendix A), for a comparison to the FT/IR spectrum of glucose. Further evidence supports this

synthesis when Figure A5, FT/IR of the gbdppz ligand, is compared to the FT/IR spectrum of the bdppz ligand (Figure A1). Similar characteristic peaks of the bdppz ligand at 700 to 1500 wavenumbers are found in both FT/IR spectra.

Section 3.3.6: Results of the synthesis of $[Pt(dione)(Cl)_4]$

Working with the ligands (dione, bdppz, and gbdppz) is often difficult due to their low solubility in most common solvents. This insolubility hindered further characterization of the ligands by other analytical means. Attaching the dione ligand to a metal center we thought would increase the solubility of the molecule because the molecule would behave more like a salt. With the dione ligand attached to the metal center, then we could build the bigger ligands, bdppz, and gbdppz. When attached to the metal center, the solubility would increase, therefore, further characterization could be conducted.

We are very confident that we were successful in synthesizing the $[Pt(dione)(Cl)_4]$ compound. The FT/IR spectrum of $[Pt(dione)(Cl)_4]$ (Figure A6) shows that a carbonyl peak is present at 1701.68 wavenumbers. When compared to Figure A22, FT/IR spectrum of the dione ligand, similar peaks and patterns of the dione ligand are present. Also in Figure A22 the carbonyl peak appears at 1682.79 wavenumbers. This shift of the carbonyl peak to 1701.68 wavenumbers in Figure A6 correlates with what is expected for a bound ligand versus a free ligand, because the metal center should cause the carbonyl peak to be shifted to a higher wavenumber.

The ^{1}H-NMR spectra (Figures C1-C3) collected further supports this synthesis. The peaks found in Figure C2 correlate with the splitting expected in the molecule. In

Figure C3, the integrations of the peaks correlate with the number of hydrogens that would be expected for each peak.

In Appendix D pages D1-D30 the crystal data reveals that this molecule has been synthesized. The crystal structure though has a 2+ metal center and a square planar configuration. We hypothesized that the DMSO used to grow the crystal could have reduced the platinum metal center from the 4+ to the 2+ oxidation state. We conducted a cyclic voltammogram (Figure F1 through F2, Appendix F) to see if the [Pt(dione)Cl_4] was 4+ when first used. The results from this test confirmed that the original product was [Pt(dione)Cl_4], and that the metal center was reduced by the DMSO during the crystal growth process.

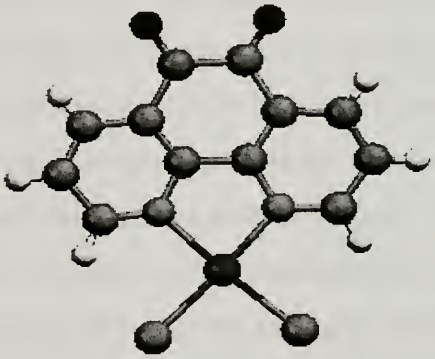


Figure 3.3.6: Ball and Stick Model of [Pt(dione)Cl_2] from Crystal Data

Section 3.3.7: Results from the synthesis of [Pt(bdppz)$(Cl)_4$]

FT/IR analysis confirms that the synthesis of [Pt(bdppz)$(Cl)_4$] was a success. The FT/IR spectrum of [Pt(bdppz)$(Cl)_4$] (Figure A7) shows a carboxyl peak at 1703.42 wavenumbers which is in the expected range. When the FT/IR spectrum of

[Pt(bdppz)(Cl)$_4$] is compared to the FT/IR spectrum of the bdppz ligand (Figure A1), peaks that are characteristic of the bdppz ligand from 700 to 1500 wavenumbers are seen in both figures. Also the carboxyl peak in Figure A7 is shifted to a higher wavenumber because of the metal center.

Section 3.3.8: Results from the synthesis of [Pd(dione)(Cl)$_4$]

Synthesis using Pd4+ as the metal center was conducted because the palladium versions of our metal based anticancer drugs were more cytotoxic than the platinum analogs.[10]

Section 3.3.8A: The synthetic scheme stirring K_2PdCl_6 and dione to make [Pd(dione)(Cl)$_4$] appears to have been successful. The FT/IR spectrum of [Pd(dione)(Cl)$_4$] (Figure A8) shows a very strong carbonyl band present at 1701.68 wavenumbers. This peak falls in the appropriate range for a carbonyl peak. Once again the carbonyl peak is shifted to a higher wavenumber in Figure A8 because of the metal center, which also supports the synthesis of this molecule. Furthermore, when the FT/IR spectrum of [Pd(dione)(Cl)$_4$] is compared to the FT/IR spectrum of the dione ligand (Figure A22) peaks that are characteristic of the dione ligand appear in both.

Section 3.3.8B: FT/IR spectrum analysis confirms that this synthesis was a failure. The attempt to synthesize the [Pd(dione)(Cl)$_4$] from the [Pd(phen)(Cl)$_4$] was a failure and the only product obtained was [Pd(phen)(Cl)$_4$], which had the same FT/IR spectrum as that in Figure A9.

Section 3.3.9: Results of the synthesis of [Pd(bdppz)(Cl)$_4$]

Spectra analysis leads us to believe that the synthesis of [Pd(bdppz)(Cl)$_4$] was a success. The FT/IR spectrum of [Pd(bdppz)(Cl)$_4$] (Figure A10) shows a carboxyl peak at

1701.30 wavenumbers, which is in the appropriate range. Also supporting this synthesis is the fact that similar characteristic bdppz peaks are found in both the FT/IR spectrum of [Pd(bdppz)$(Cl)_4$] and the FT/IR spectrum of the bdppz ligand (Figure A1).

Section 3.3.10: Results of the synthesis of [Pd(gbdppz)$(Cl)_4$]

FT/IR analysis leads to the belief that the synthesis of [Pd(gbdppz)$(Cl)_4$] was a success. The FT/IR spectrum of [Pd(gbdppz)$(Cl)_4$] (Figure A11) has a carbonyl peak at 1728.30 wavenumbers, which is in the appropriate range. When the FT/IR spectrum of [Pd(gbdppz)$(Cl)_4$] is compared to the FT/IR spectrum of glucose, Figure A23, the broad OH peaks expected from the glucose molecule are found in both figures.

Section 3.3.11: Results of the synthesis of [Pd(dione-glucosamine)$(Cl)_4$]

Glucose was replaced by glucosamine as the nutrient to attach to the molecules because with glucosamine we were better able to predict where the condensation reaction with dione or a carboxylic acid would occur.

The FT/IR data and ^{1}H-NMR data collected supported the synthesis of [Pd(dione-glucosamine)$(Cl)_4$]. The FT/IR spectrum of [Pd(dione-glucosamine)$(Cl)_4$] (Figure A12) has a carbonyl peak at 1701.68 wavenumbers, which is in the expected range. This spectrum also has similar peaks that are found in the FT/IR spectrum of glucosamine, Figure A24 (Appendix A).

Further support that the glucosamine was attached to the [Pd(dione)$(Cl)_4$] molecule is found in the ^{1}H-NMR spectra (Figures C4-C5) of the molecule. In C4, the peaks and integrations correlate with what would be expected for [Pd(dione-glucosamine)$(Cl)_4$]. In Figure C5 D_20 has been added to the molecule. D_2O causes the peaks that arise from the OH groups present on the glucosamine to disappear. When

Figure C5 is compared to Figure C4,the 1H-NMR without D_2O, four peaks are missing in Figure C5. This difference confirms that the glucosamine was attached to the molecule.

The High Resolution Mass Spec data, though reveals that the synthesis of [Pd(dione-glucosamine)$(Cl)_4$] was not successful. The Mass Spectra of [Pd(dione-glucosamine)$(Cl)_4$] (Figures E1-E4) reveal that the molecule has a molecular weight in the thousands. This molecular weight is many times larger than the molecular weight that is to be expected. These data support the idea that either the glucosamine polymerized or that there are multiple metal centers present that are forming dimers and trimers. Attempts at crystal growth have been unsuccessful.

Section 3.3.12: Results of the synthesis of $[Pd(dione)_2]Cl_2$

Pd 2+ was used in place of Pd 4+ as the metal center because once again solubility problems were encountered with characterization. The use of Pd 2+ would enable the molecule to be square planar as opposed to octahedral.

The FT/IR data of $[Pd(dione)_2]Cl_2$ (Figure A13) suggests that this synthesis was successful. The FT/IR spectrum shows a very strong carbonyl peak at 1705.73 wavenumbers. Similar peaks that are characteristic to the dione ligand are found in both the FT/IR spectrum of $[Pd(dione)_2(Cl)_2]$ (Figure A13) and the FT/IR spectrum of dione (Figure A22), which further supports the success of the synthesis.

The ^{1}H-NMR spectra (C6) of $[Pd(dione)_2]Cl_2$ also support the synthesis. The peaks correlate with the splitting pattern expected from the molecule. The integrations also correlate with the number of hydrogens expected for each peak.

The High Resolution Mass Spectra (Figures E5 through E8), though, do not support this synthesis. These figures reveal that the molecule has a molecular weight in

the thousands. This molecular weight is many times larger than the molecular weight that is to be expected. This data supports the idea that there are multiple metal centers present that are forming dimers and trimers.

Section 3.3.13: Results of the synthesis of $[Pd(dione\text{-}glucosamine)_2]Cl_2$

The FT/IR spectrum of $[Pd(dione\text{-}glucosamine)_2]Cl_2$ (Figure A14) supports this synthesis. The FT/IR spectrum shows a carbonyl peak in the expected range at 1699.76 wavenumbers and peaks that are characteristic to the glucosamine peaks found in Figure A24.

The ^{1}H-NMR spectra of $[Pd(dione\text{-}glucosamine)_2]Cl_2$ (Figures C7-C8) also confirm this synthesis. In the NMR spectrum, Figure C7, the peaks correlate with the splitting pattern expected from the molecule. The integrations also correlate with the number of hydrogens expected for each peak. In Figure C8 D_20 has been added to the molecule. D_2O causes the peaks that arise from the OH groups present on the glucosamine to disappear. When Figure C8 is compared to Figure C7, four peaks are missing in Figure C8. This difference confirms that the glucosamine was attached to the molecule.

The High Resolution Mass Spectra of $[Pd(dione\text{-}glucosamine)_2]Cl_2$ (Figures E9 through E12), though, do not support the synthesis of this molecule. These figures reveal that the molecule has a molecular weight in the thousands. This molecular weight is many times larger than the molecular weight that is to be expected. These data support the idea that either the glucosamine polymerized or that there are multiple metal centers present that are forming dimers and trimers.

Section 3.3.14: Results of synthesis of $[Pd(bdppz)_2]Cl_2$

FT/IR analysis of $[Pd(bdppz)_2]Cl_2$ supports this synthesis. The FT/IR spectrum of $[Pd(bdppz)_2]Cl_2$ (Figure A15) has a carboxyl peak at 1727.72 wavenumbers, which is a little higher than the expected range of 1680 to 1720 wavenumbers. Though this is higher than the expected range, Figure A15 does have peaks that are characteristic to those found in the bdppz ligand, Figure A1. The far shift may be due to the metal center.

The High Resolution Mass Spectra of $[Pd(bdppz)_2(Cl)_2]$ (Figures E13 through E16) do not support this synthesis. These figures reveal that the molecule has a molecular weight in the thousands. This molecular weight is many times larger than the molecular weight that is to be expected. These data support the idea that there are multiple metal centers present that are forming dimers and trimers.

Section 3.3.15: Results of the synthesis of $[Pd(bdppz\text{-}glucosamine)_2]Cl_2$

The FT/IR spectrum of $[Pd(bdppz\text{-}glucosamine)_2]Cl_2$ (Figure A16) confirms this synthesis because it shows a carbonyl peak in the expected range at 1703.42 wavenumbers and peaks that are characteristic to the glucosamine peaks found in Figure A24.

The ^{1}H-NMR spectra of $[Pd(bdppz\text{-}glucosamine)_2]Cl_2$ (Figures C9 and C10) also support this synthesis. In Figure C9, the peaks correlate with the splitting pattern expected from the molecule. The integrations also correlate with the number of hydrogens expected for each peak. In Figure C10 D_2O has been added to the molecule. D_2O causes the peaks that arise from the OH groups present on the glucosamine to disappear. When Figure C10 is compared to Figure C9, four peaks are missing in Figure C10. This difference confirms that the glucosamine was attached to the molecule.

The High Resolution Mass Spectra (Figures E17 through E21), though, do not support this synthesis. These figures reveal that the molecule has a molecular weight in the thousands. This molecular weight is many times larger than the molecular weight that is to be expected. These data support the idea that either the glucosamine polymerized or that there are multiple metal centers present that are forming dimers and trimers.

Section 3.3.16: Results of synthesis of $[Pt(dione)_2(PF_6)_2]$

Evidence supporting the idea of multiple metal centers led synthesis to be conducted with Pt 2+. In the past platinum has been easier to characterize.

Section 3.3.16A: The attempted synthesis of $[Pt(dione)_2](PF_6)_2$ using Ag_3Citrate was a failure because no product was obtained. It is believed that the Ag_3Citrate had decomposed.

Section 3.3.16B: The synthesis of $[Pt(dione)_2](PF_6)_2$ using Ag_2Tartrate was also a failure. A brown precipitate was collected and the FT/IR spectrum of $[Pt(dione)_2](PF_6)_2$, Figure A17, shows a carbonyl peak present in the appropriate range at 1693.20 wavenumbers. The product, though, was very waxy and sticky and was not conducive to further research or analysis.

Section 3.3.17: Results of the synthesis of $[Pt(dione)_2]Cl_2$

FT/IR analysis of $[Pt(dione)_2(Cl)_2]$ supports this synthesis. The FT/IR spectrum of $[Pt(dione)_2]Cl_2$ (Figure A18) shows a carbonyl peak at 1702.46 wavenumbers. This peak is in the expected range. Also the spectrum has similar peaks from 1000 to 1500 wavenumbers that are found in the dione ligand spectrum in Figure A22.

Section 3.3.18: Results of the attempted synthesis of $[Pt(dione)_2](ClO_4)_2$

This synthesis was a failure because no product could be obtained.

Section 3.3.19: Results of the synthesis of $[Pt(dione)_2](NaBPh_4)_2$

This synthesis was a failure. The product turned gray, black on the vac-line. Usually this indicates that the metal center has been reduced or that the product has decomposed.

Section 3.3.20: Results of the synthesis of $[Pt(dione)_2(Tartrate)]$

FT/IR analysis strongly suggests that $[Pt(dione)_2(Tartrate)]$ has been synthesized. The FT/IR spectrum of $[Pt(dione)_2(Tartrate)]$ (Figure A19) has a carbonyl peak present at 1693.97 wavenumbers. This peak falls in the appropriate carbonyl range. The spectrum also has a broad peak in the OH range of 3000 to 3500 wavenumbers. When compared to Figure A26, the FT/IR spectrum of $Ag_2Tartrate$, this is where the expected OH peaks from the tartrate should fall. The FT/IR spectrum of $[Pt(dione)_2(Tartrate)]$ also has peaks that are characteristic of the other tartrate peaks found in Figure A26. Further evidence to support this synthesis is found when the FT/IR spectrum of $[Pt(dione)_2(Tartrate)]$ is compared to the FT/IR spectrum of the dione ligand, Figure A22. Both spectra have peaks that are characteristic of the dione ligand. These results imply that the dione is attached to the metal center and that the tartrate is acting as a counterion.

The NMR spectra, Figures C11 to C13, of this molecule also confirm this synthesis. d-DMSO was used for the solvent in these NMR investigations. Figure C11 is a ^{1}H-NMR of $[Pt(dione)_2(Tartrate)]$. The peaks and integrations correlate with what would be expected for the mono or bis dione ligand attached to a metal center. Figures C12 and C13 are ^{13}C-NMR and show that six carbon peaks are present, which would be expected for the mono or bis dione ligand. No tartrate peaks appear in these spectra.

When running this experiment, a white precipitate formed when the compound was placed in the d-DMSO. This precipitate was filtered off and then the NMR was taken. We believe that the d-DMSO reduced the metal center, which caused the tartrate to precipitate. We believe this explains why no tartrate peaks are present. This same reduction was encountered and found during the re-crystallization of the [Pt(dione)Cl_4]. These results though support the idea that the dione is attached to the metal center and that the tartrate is acting as a counterion.

Section 4: Metal Based CO_2 Reduction Catalyst: Background, Synthesis, Results & Conclusions

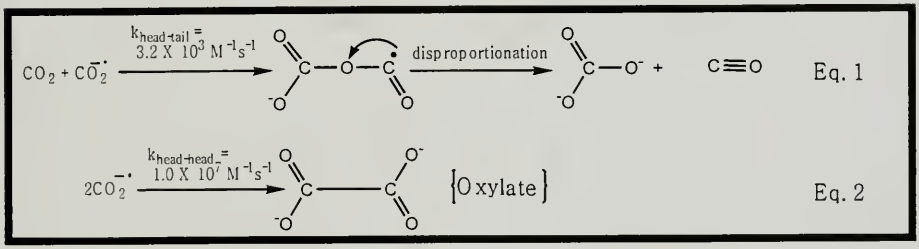
Section 4.1: Metal Based CO_2 Reduction Catalyst: Background

During photosynthesis plants use atmospheric CO_2, water, and visible light to produce complex molecules containing carbon-carbon bonds. An iron-sulfur compound is the catalytic site of the enzyme, or biological catalyst, that helps to form these carbon-carbon bonds during photosynthesis.

Several research groups are trying to create different CO_2 reduction catalysts that would form carbon-carbon bonds. A CO_2 reduction catalyst would be very beneficial in dealing with the by-product of aerobic respiration, specifically CO_2, in closed environments where no plants are present, such as in submarines and space stations. In a closed environment, aerobic respiration releases CO_2 into the atmosphere. Current technology uses "scrubbers" to deal with the by-products of aerobic respiration (CO_2) in closed environments. These scrubbers trap the CO_2. These scrubbers soon become saturated and need to be either replaced or recharged. A system that both removes the

CO_2 from the atmosphere in a continuous fashion and produces useful organic materials, i.e carbon-carbon bond molecules, would be ideal.

In order to make this type of catalyst, two CO_2 radical anions (CO_2*-) must bind together (Eq. 2 in Scheme 4.1). The conditions necessary for the combination of two CO_2*- radicals is very hard to create because usually the number of CO_2*- radicals present are few compared to the number of CO_2 normal molecules. Since more CO_2 normal molecules are present, the CO_2*- usually reacts with the CO_2. This synthesis does not result in the formation of carbon-carbon bonds (Eq.1 in Scheme 4.1)



Scheme 4.1: The Different Synthesis that a CO_2*- Can Undergo

To date there is only one CO_2 reduction catalyst that holds much promise in creating carbon-carbon bonds. This catalyst was developed by Dr. Clifford Paul Kubiak.[11] This catalyst has two metal catalytic centers that are very close to one another. The metal centers are connected through a carbon chain. This closeness increases the possibility that a CO2*- will find another CO2*- before it finds a normal CO_2. This arrangement enables more CO2*- radicals to bind to each other, thus forming carbon-carbon bonds.

Dr. Granger's researchers have designed a superior catalytic system for the formation of carbon-carbon bonds from CO_2. This catalyst has two catalytic sites on the

same metal center and the compound forms an octahedrally coordinated metal bidentate ligand complex. This configuration places the catalytic centers much closer than on Kubiak's molecule. This arrangement increases the potential for the CO_2*- radicals to bind to each other. With this configuration the carbon-carbon bond compounds form more readily and at a faster rate. This catalyst has two bidentate ligands, di-2-pyridolketone (dpk), that contain a ketone functional group, carbonyl, that readily adds CO_2 (Figure 4.1).

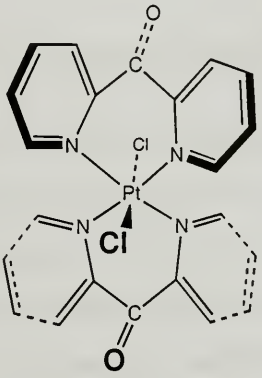


Figure 4.1: Catalyst [Pt(dpk)$_2$Cl$_2$]

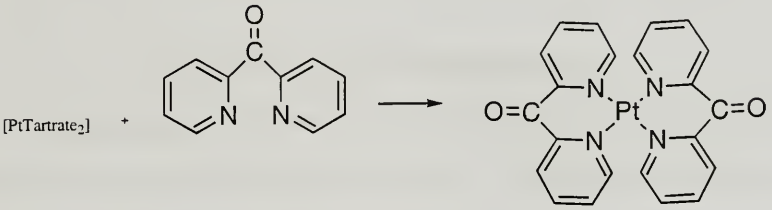
This compound contains a platinum metal center that is ideally suited to serve as a 2-electron transfer agent to facilitate the simultaneous production of two CO_2*- radicals.

The research in this thesis focuses on enhancing the catalytic properties of the catalyst by synthesizing a compound with a platinum 2+ metal center. This change from the platinum 4+ to the platinum 2+ could increase the rate at which the CO_2*- radicals are formed therefore increasing the amount of carbon-carbon bond compounds made.

Section 4.2: Metal Based CO_2 Reduction Catalyst: Synthesis

Section 4.2.1: Synthesis of [Pt(di-2-pyridolketone)$_2$(PF$_6$)$_2$]

$$K_2PtCl_4 \quad + \quad Ag_2Tartrate \longrightarrow [PtTartrate_2]$$

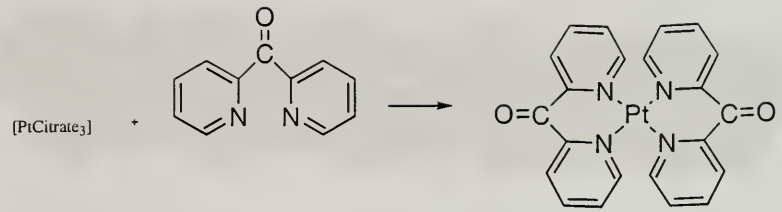


Scheme 4.2.1: Synthesis of [Pt(dpk)$_2$(PF$_6$)$_2$]

K_2PtCl_4 was dissolved in ultra pure water and an equimolar amount of Ag_2Tartarate was added. A pinkish solution formed. This solution was left to stir for 4 to 5 hours and then was refluxed until the solution turned a very light brownish color. The solution was then filtered through celite® and a pale, pale yellow filtrate was collected. A 2:1 ratio of di-2-pyridolketone (dpk) was added to the pale yellow filtrate and stirred until all dissolved. Then a 2:1 ratio of KPF_6 salt was added and a yellowish precipitate formed. This precipitate was filtered and collected on a frit. Then the precipitate was left on the vac-line to dry. Next the precipitate was re-crystallized by dissolving the precipitate in acetone and precipitating it out with ether. A pale yellow precipitate was then collected on a frit and dried under vacuum. An FT/IR spectrum (Figure A20, Appendix A) was taken of the product. A crystal suitable for analysis was obtained through slow diffusion of acetone and ether (Figures D30-D50, Appendix D).

Section 4.2.2: Synthesis of [Pt(dpk)$_2$(PF$_6$)$_2$]

$$K_2PtCl_4 \quad + \quad Ag_3Citrate \longrightarrow [PtCitrate_3]$$



Scheme 4.2.2: Synthesis of $[Pt(dpk)_2(PF_6)_2]$

The same procedure as in Section 4.1 can be followed using equimolar silver to chloride amounts of $Ag_3Citrate$ instead of $Ag_2Tartrate$. An FT/IR spectrum (Figure A21, Appendix A) was taken of the pale yellow product formed from this reaction.

Section 4.3: Metal Based CO_2 Reduction Catalyst: Results and Conclusions

Section 4.3.1: Results from the synthesis of $[Pt(dpk)_2(PF_6)_2]$ using $Ag_2Tartrate$

The FT/IR spectrum of $[Pt(dpk)_2(PF_6)_2]$ imply that the synthesis was a success. The FT/IR spectrum of $[Pt(dpk)_2(PF_6)_2]$ (Figure A20) has a carbonyl peak in the expected range at 1681.44 wavenumbers. Also the FT/IR spectrum of $[Pt(dpk)_2(PF_6)_2]$ has peaks that are characteristic of the peaks of the dpk ligand found in Figure A25 (Appendix A).

The crystallographic data obtained, Figures D30-D50 (Appendix D), reveal that the compound synthesized is a polymer with a palladium metal center, $[Pd(dpk)_2(PF_6)]n$. These results were very interesting because the metal material for the synthesis was K_2PtCl_4. We questioned how the metal center could be palladium. We used the flame method on the atomic absorption spectrometer to conduct a qualitative analysis to determine if platinum and palladium were both present in the metal starting material. The results from the atomic absorption spectrometer roughly speaking revealed that the starting material was 50:50 platinum to palladium.

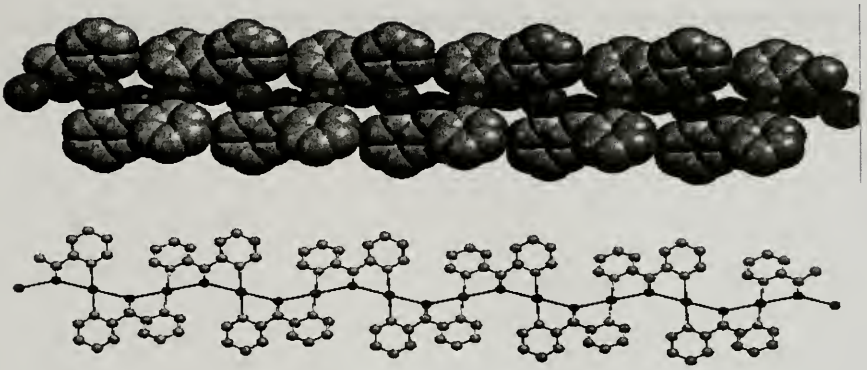


Figure 4.3.1: Models of $[Pt(dpk)_2(PF_6)]n$ Polymer from Crystal Data

Section 4.3.2: Results from the synthesis of $[Pt(dpk)_2(PF_6)_2]$ using $Ag_3Citrate$

Spectral analysis confirms that this product can be used using both $Ag_3Citrate$ and $Ag_2Tartrate$. The FT/IR spectrum of $[Pt(dpk)_2(PF_6)_2]$ using $Ag_3Citrate$ (Figure A21) supports this synthesis because a carbonyl peak is present at 1682.01 wavenumbers, which falls in the appropriate range. Also Figure A21 has peaks that are characteristic to the dpk ligand, Figure A25. The carbonyl peak in the FT/IR spectrum of $[Pt(dpk)_2(PF_6)_2]$ using $Ag_3Citrate$ is less than one wavenumber away from the carbonyl peak found in the FT/IR spectrum of $[Pt(dpk)_2(PF_6)_2]$ using $Ag_2Tartrate$, Figure A20. This difference implies that the same molecule was made using both the $Ag_3Citrate$ and the $Ag_2Tartrate$.

Section 5: Further Research

Further research can be conducted in many different areas. A crystal structure needs to be obtained for the $[Pt(dione)Cl_4]$ that has a 4+ platinum metal center. Further characterization needs to be conducted on the $[Pt(dione)_2]Cl_2$ and on the

[Pt(dione)$_2$(Tartrate)] molecules. Further investigation into the starting material K_2PtCl_4 also needs to be conducted.

Appendix A
FT/IR Spectra

Appendix A
FTIR Spectra

Figure A1: FT/IR of bdppz

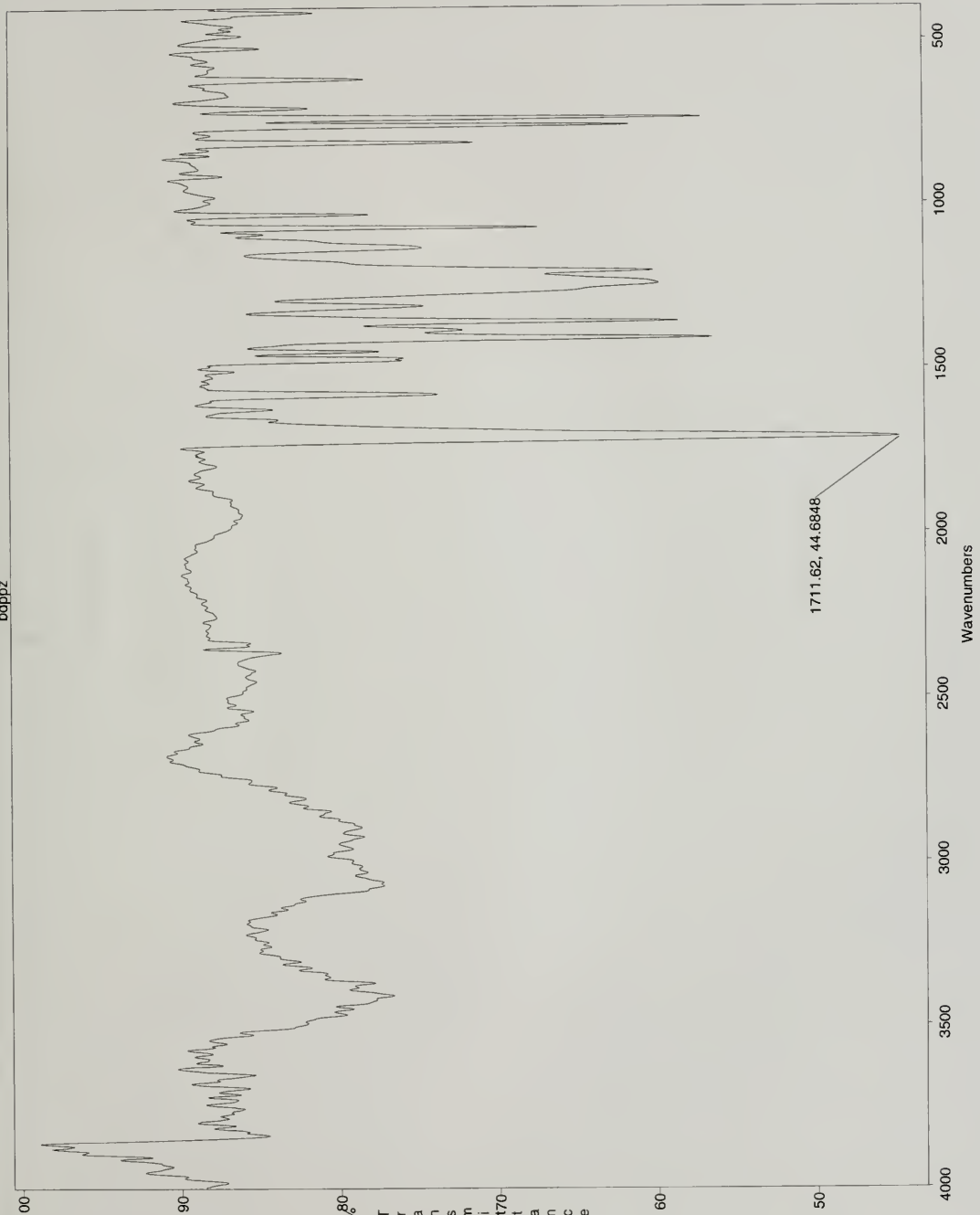
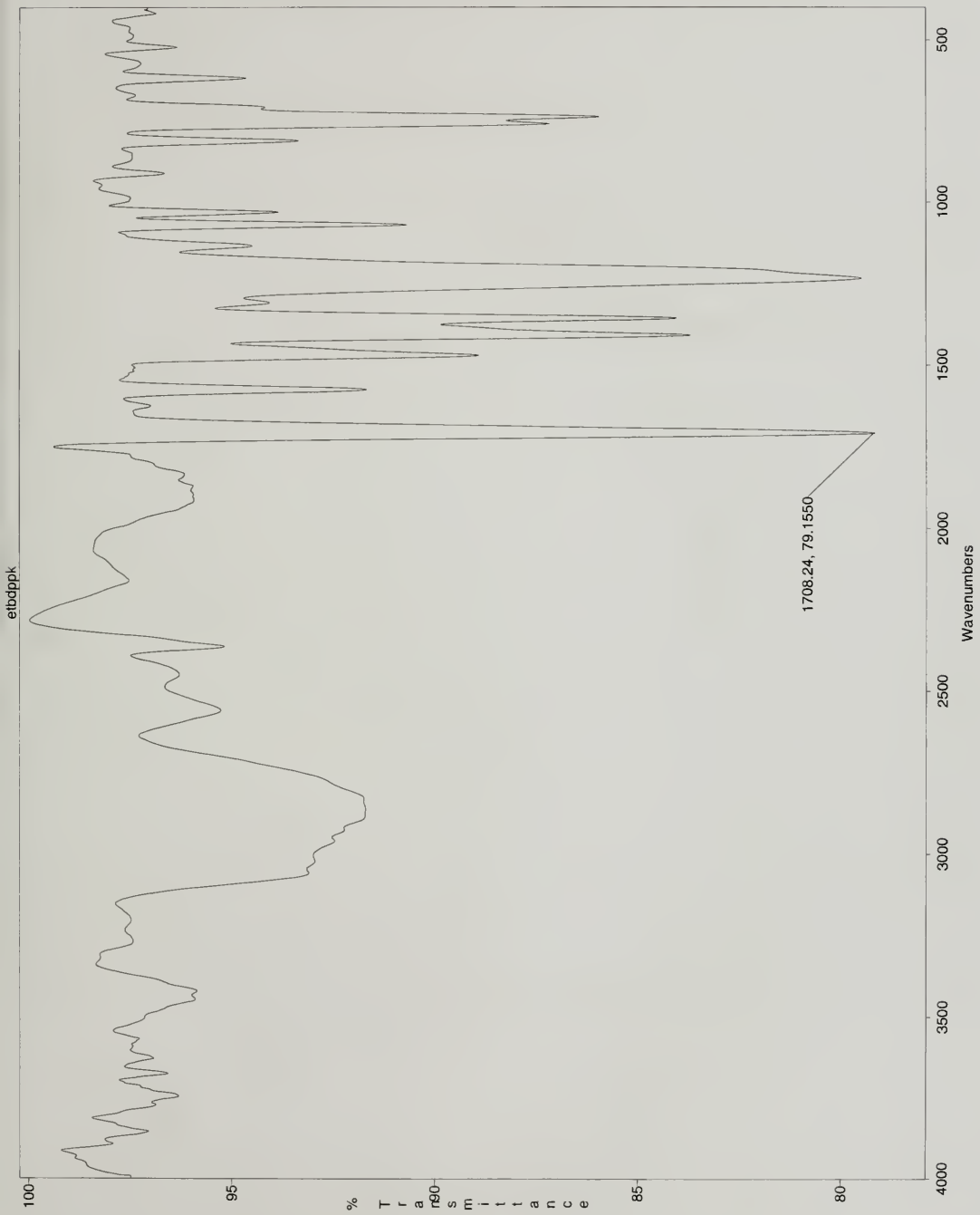


Figure A2: FT/IR of ethyl-bdppz
(dione & 3,4-diaminobenzoic acid in ethanol)



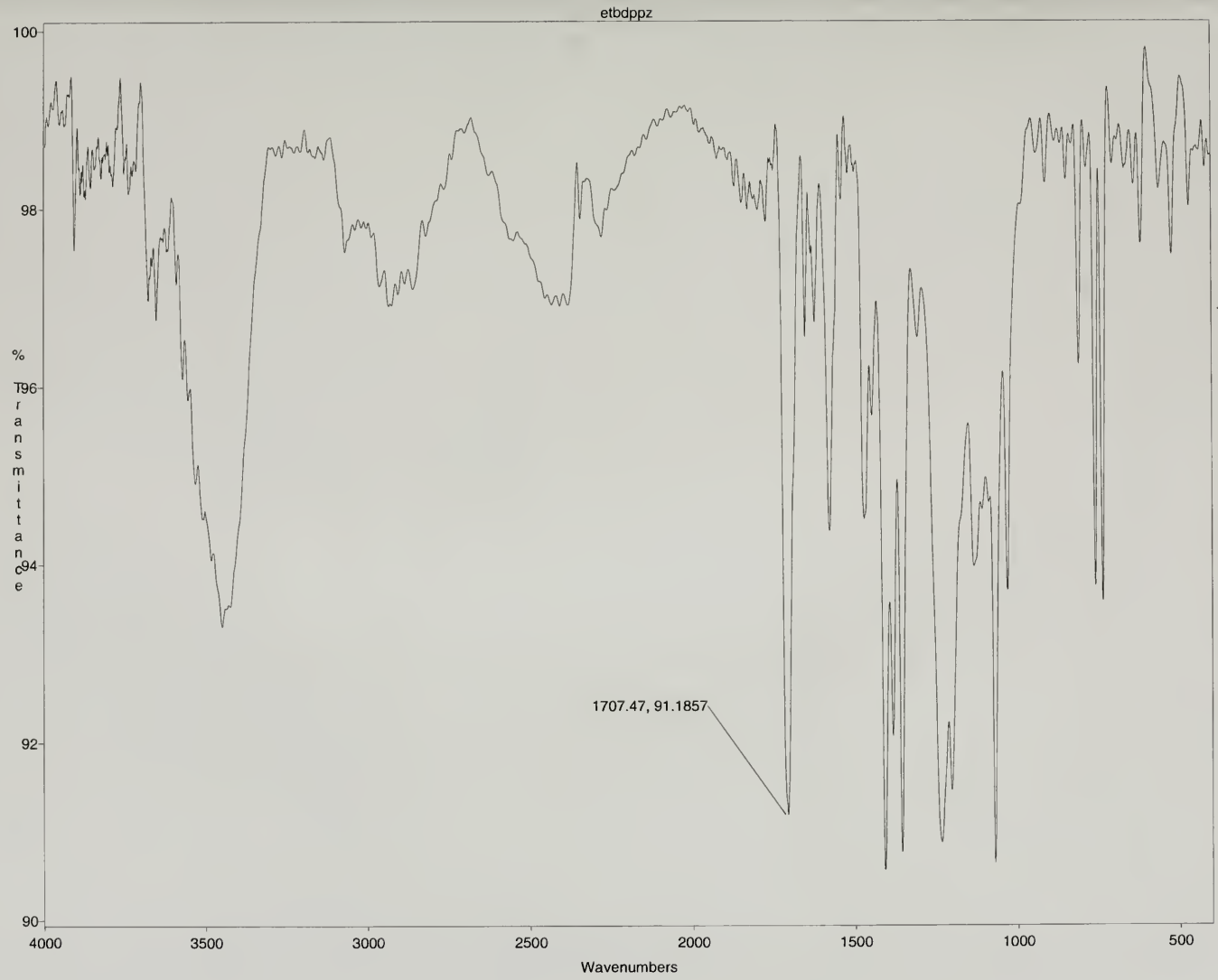


Figure A3: FT/IR of ethyl-bdppz (bdppz in ethanol)

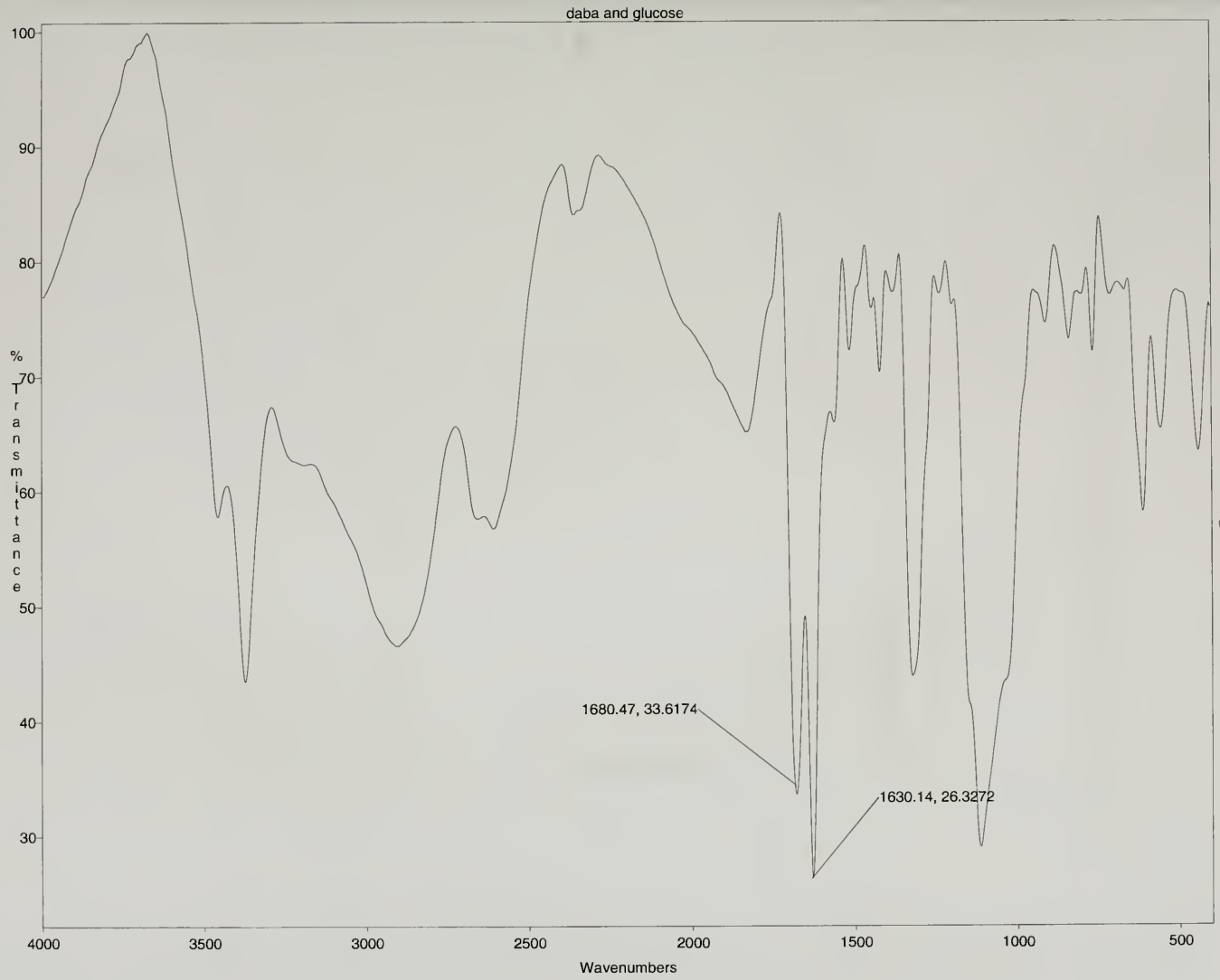
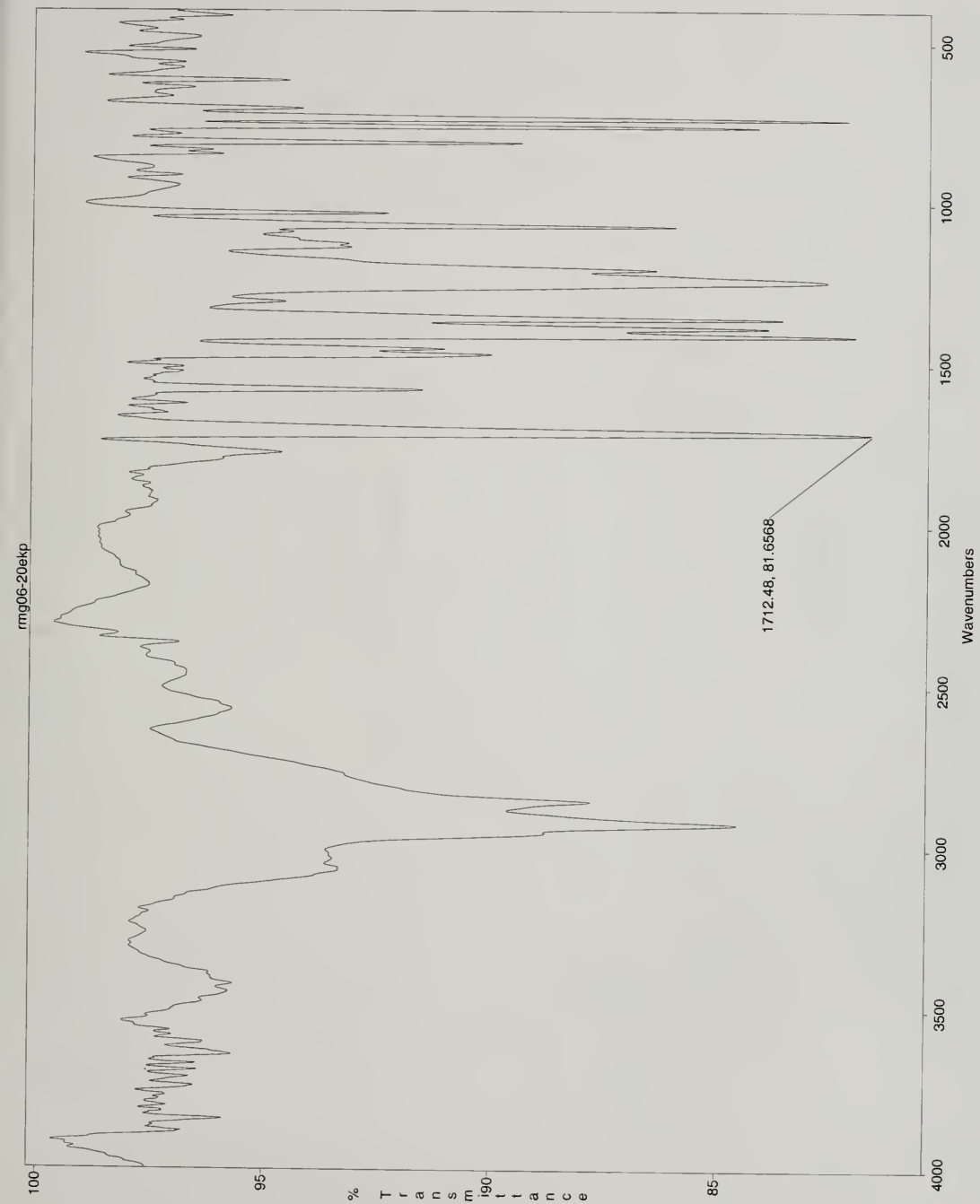


Figure A4: FT/IR of 3,4-diaminobenzoic acid-glucose

Figure A5: FT/IR of gbdppz



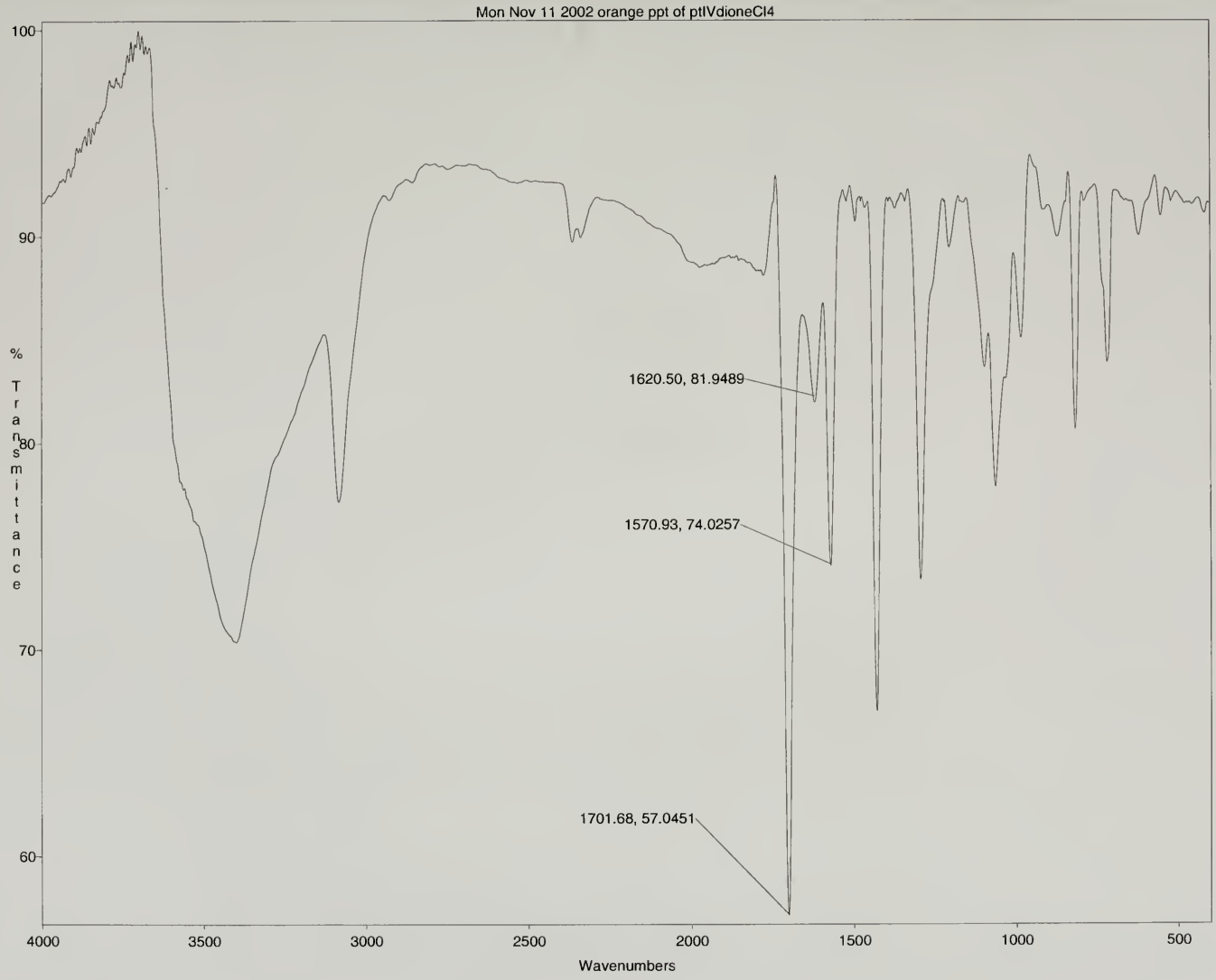


Figure A6: FT/IR of [Pt(dione)Cl4]

A6

Figure A7: FT/IR of [Pt(bdppz)Cl4]

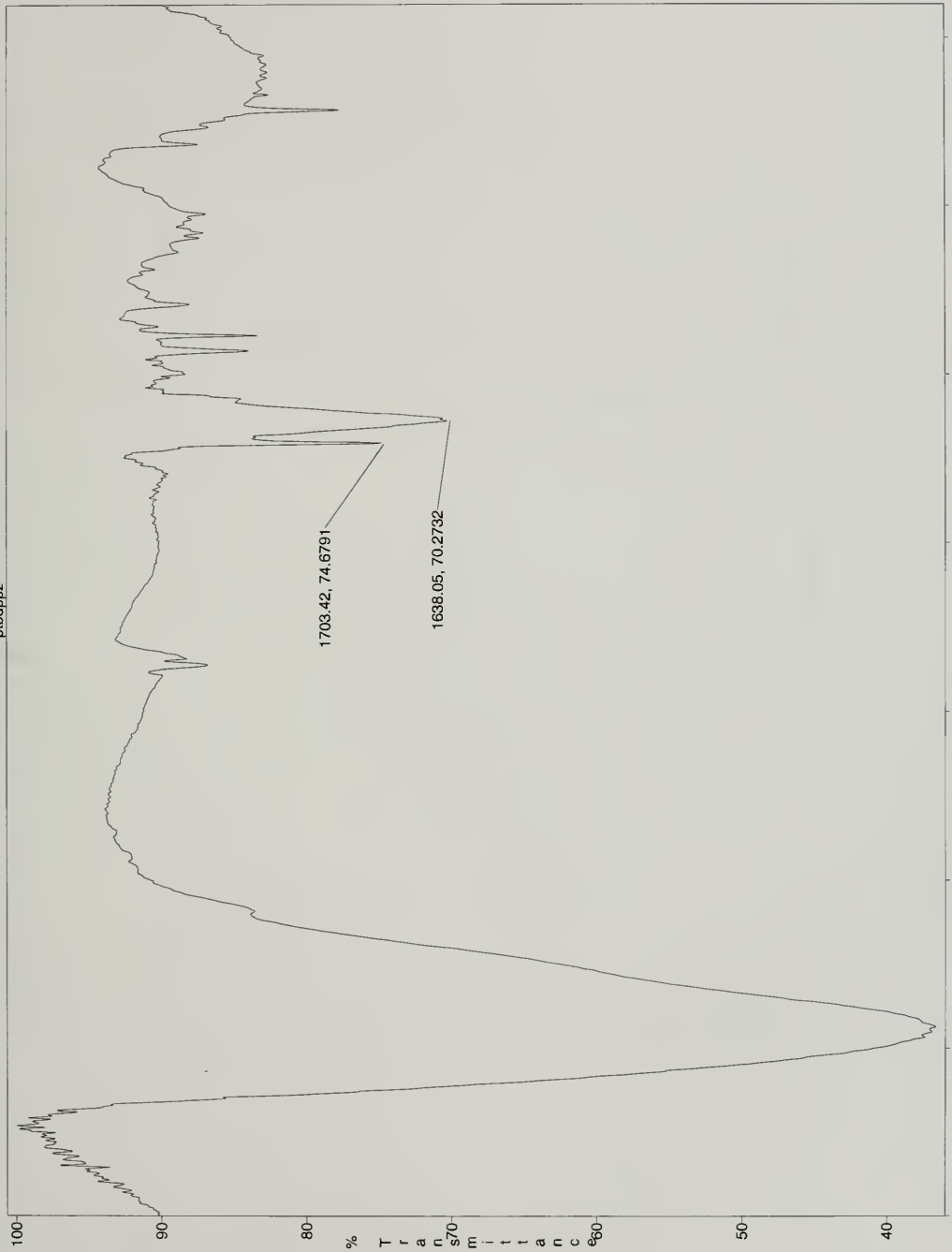
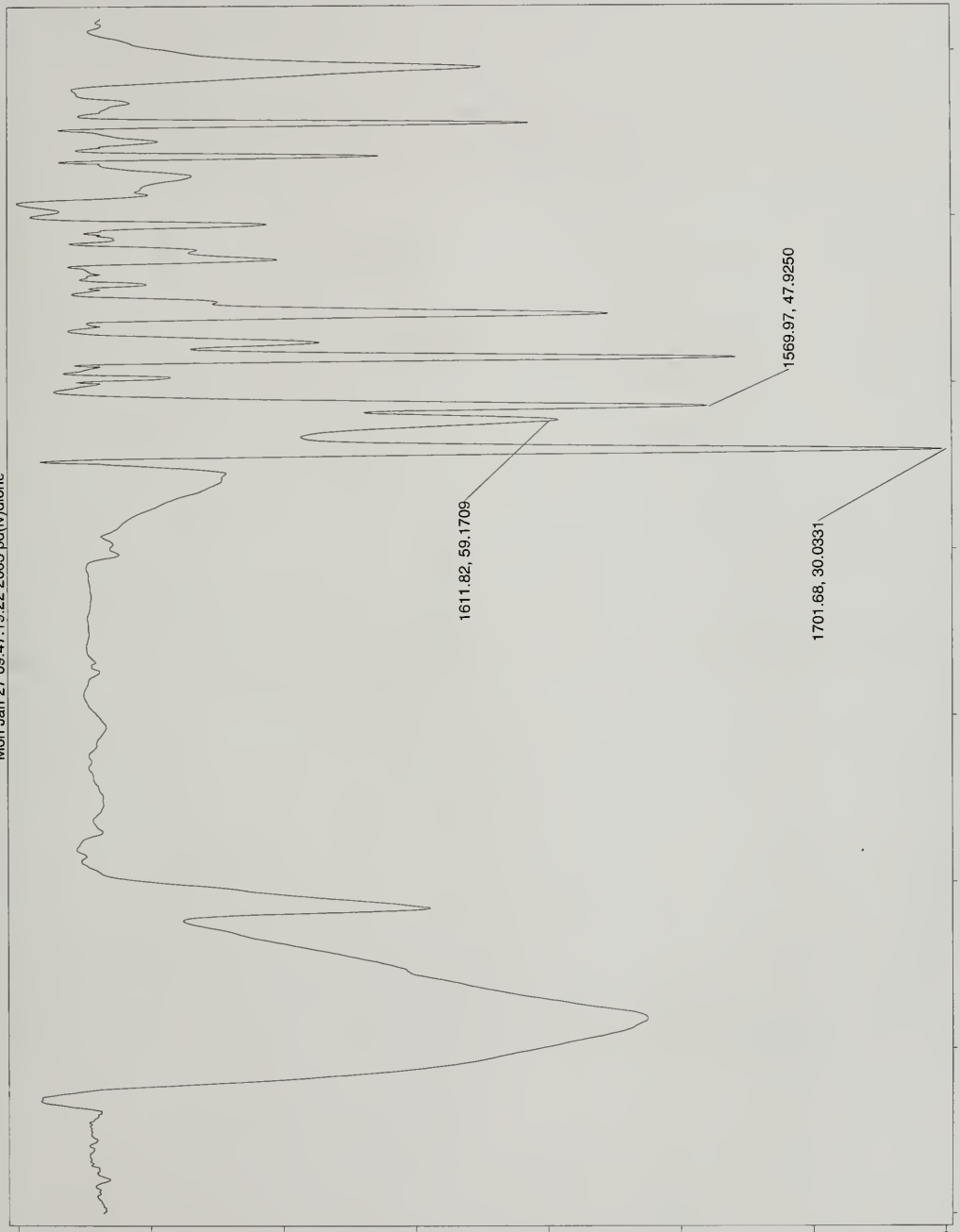


Figure A8: FT/IR of [Pd(dione)Cl4]



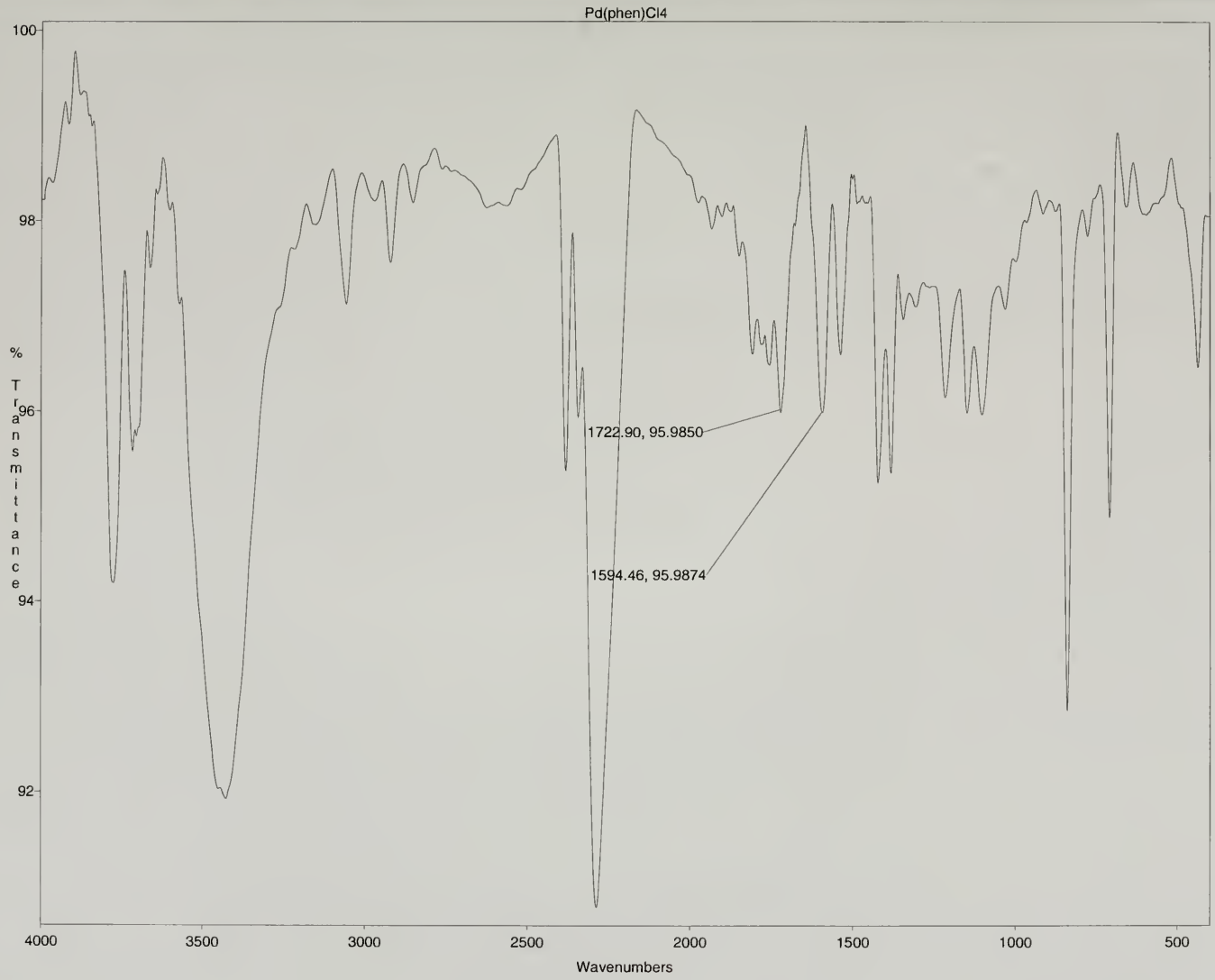


Figure A9: FT/IR of [Pd(phen)Cl4]

A9

Figure A10: FT/IR of [Pd(bdppz)Cl4]

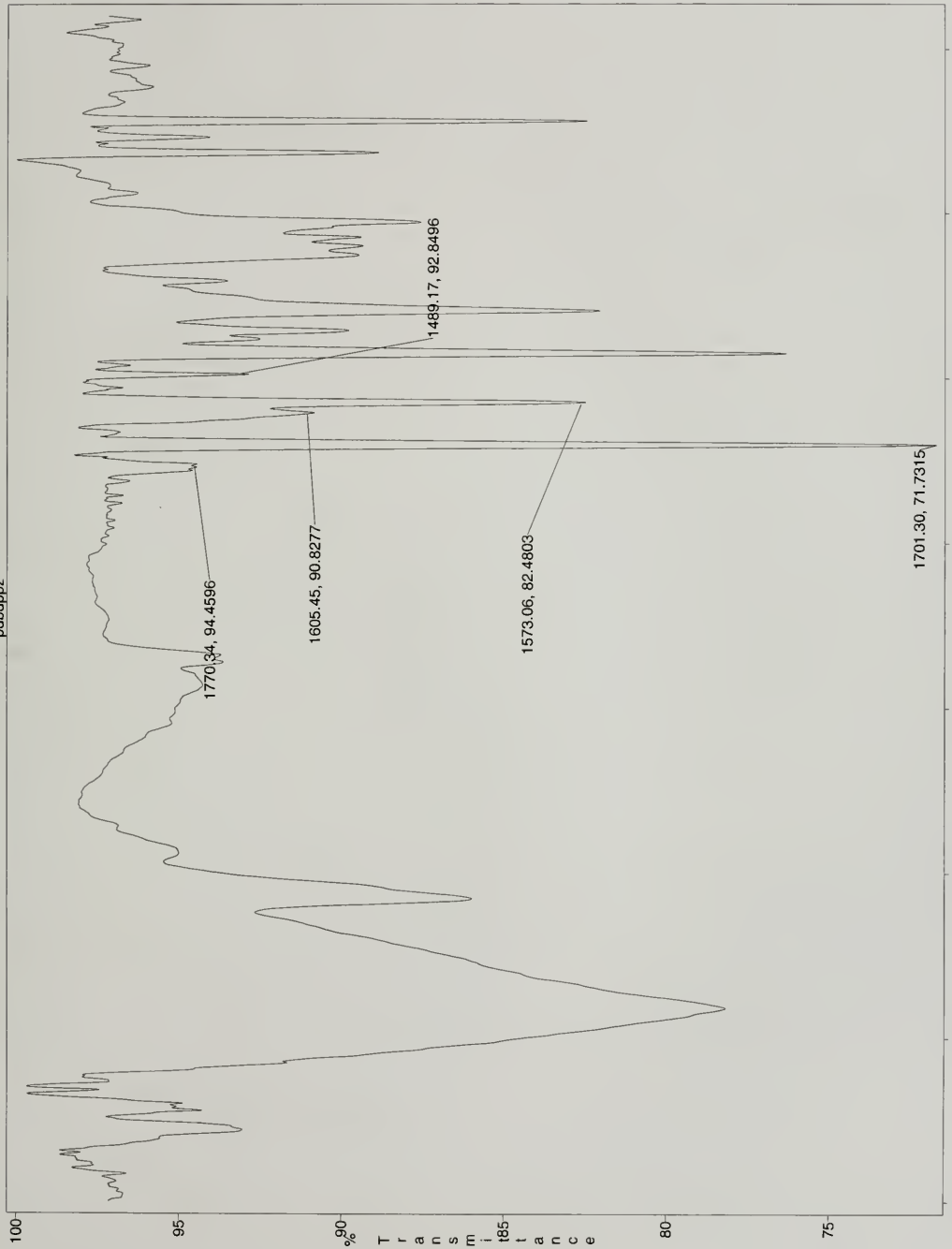


Figure A11: FT/IR of [Pd(gbdppz)Cl4]

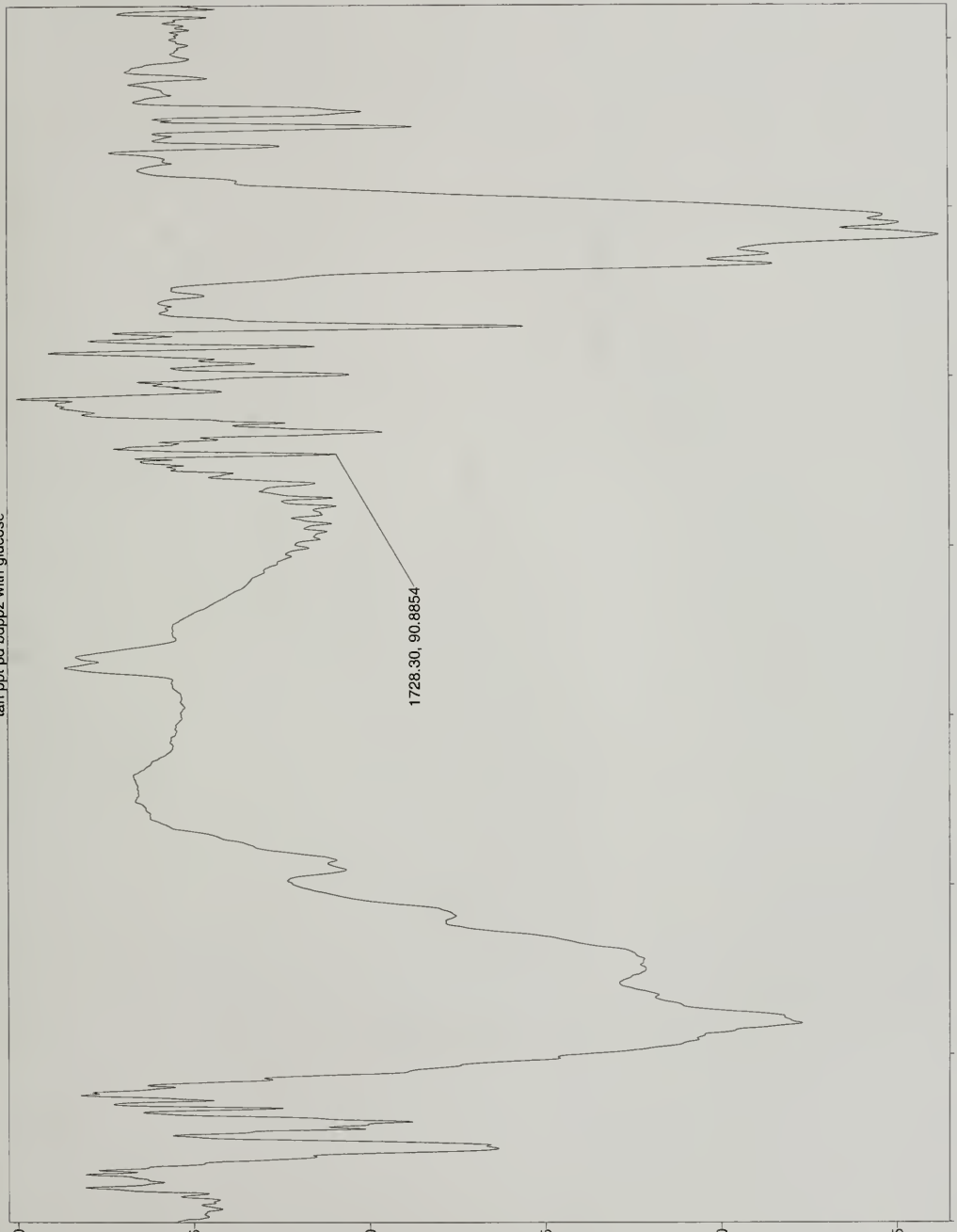


Figure A12: FT/IR of [Pd(dione-glucosamine)Cl4] A12

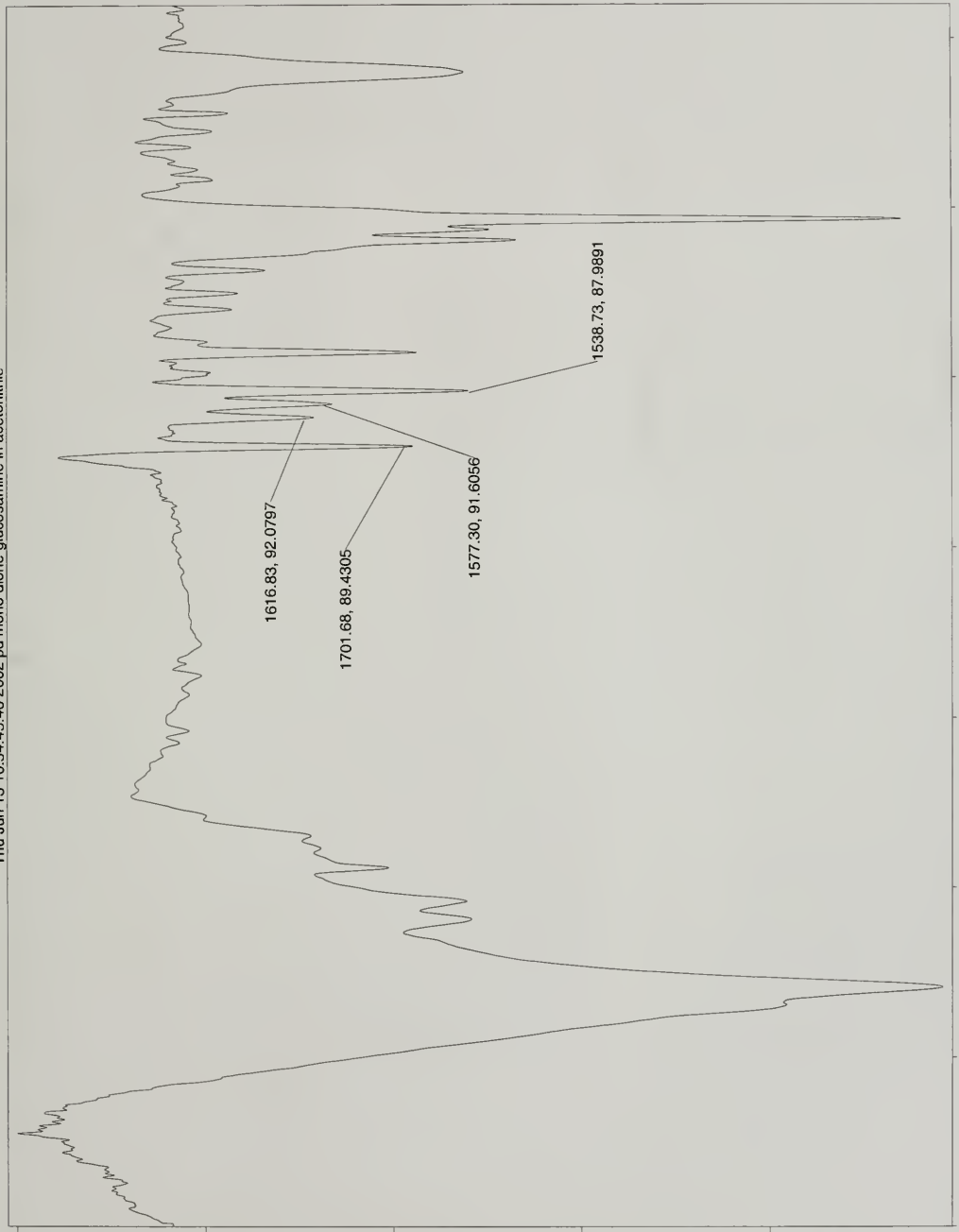


Figure A13: FT/IR of $[Pd(dione)_2Cl_2]$

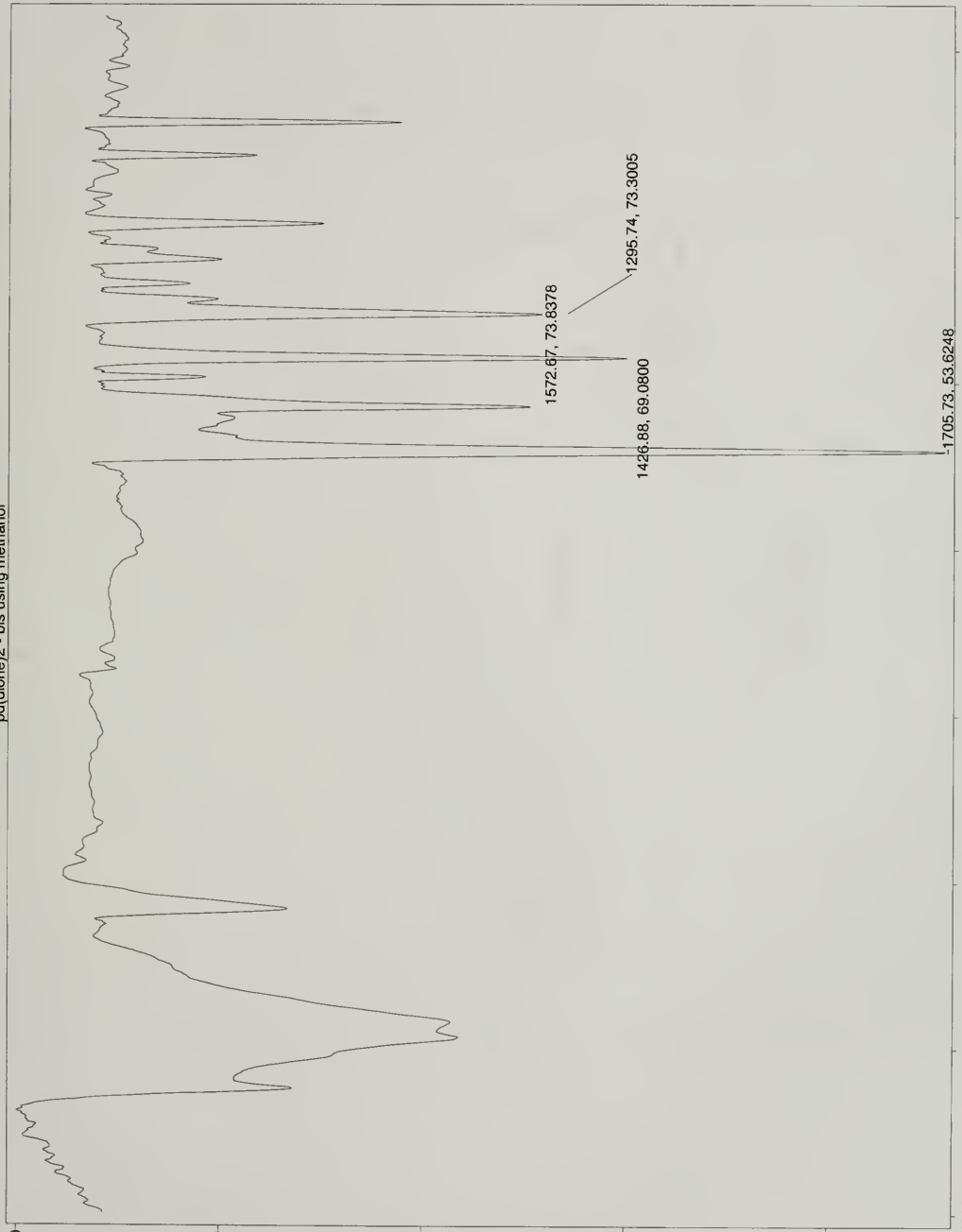


Figure A14: FT/IR of [Pd(dione-glucosamine)$_2$Cl$_2$] A14

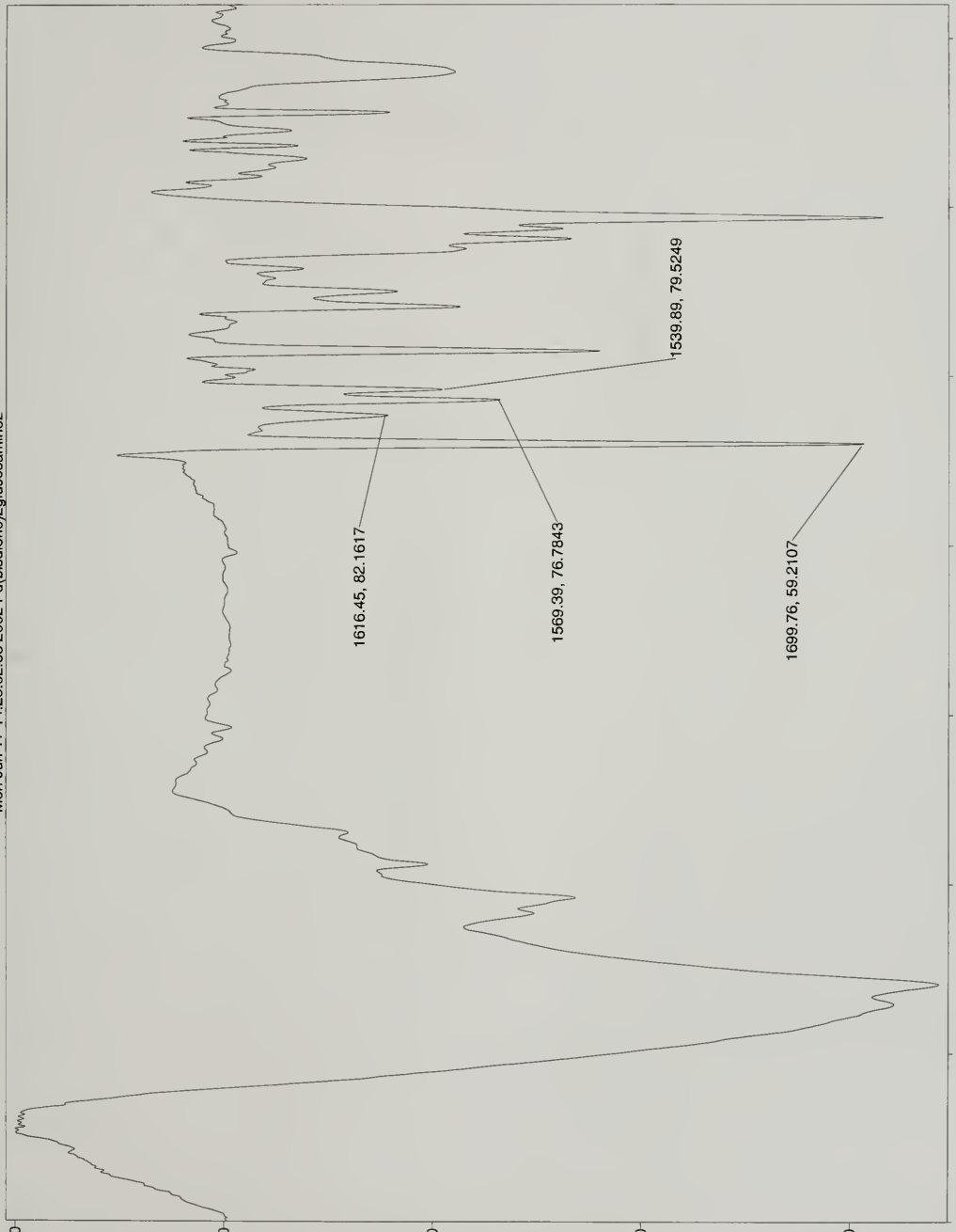


Figure A15: FT/IR of [Pd(bdppz)Cl$_2$]

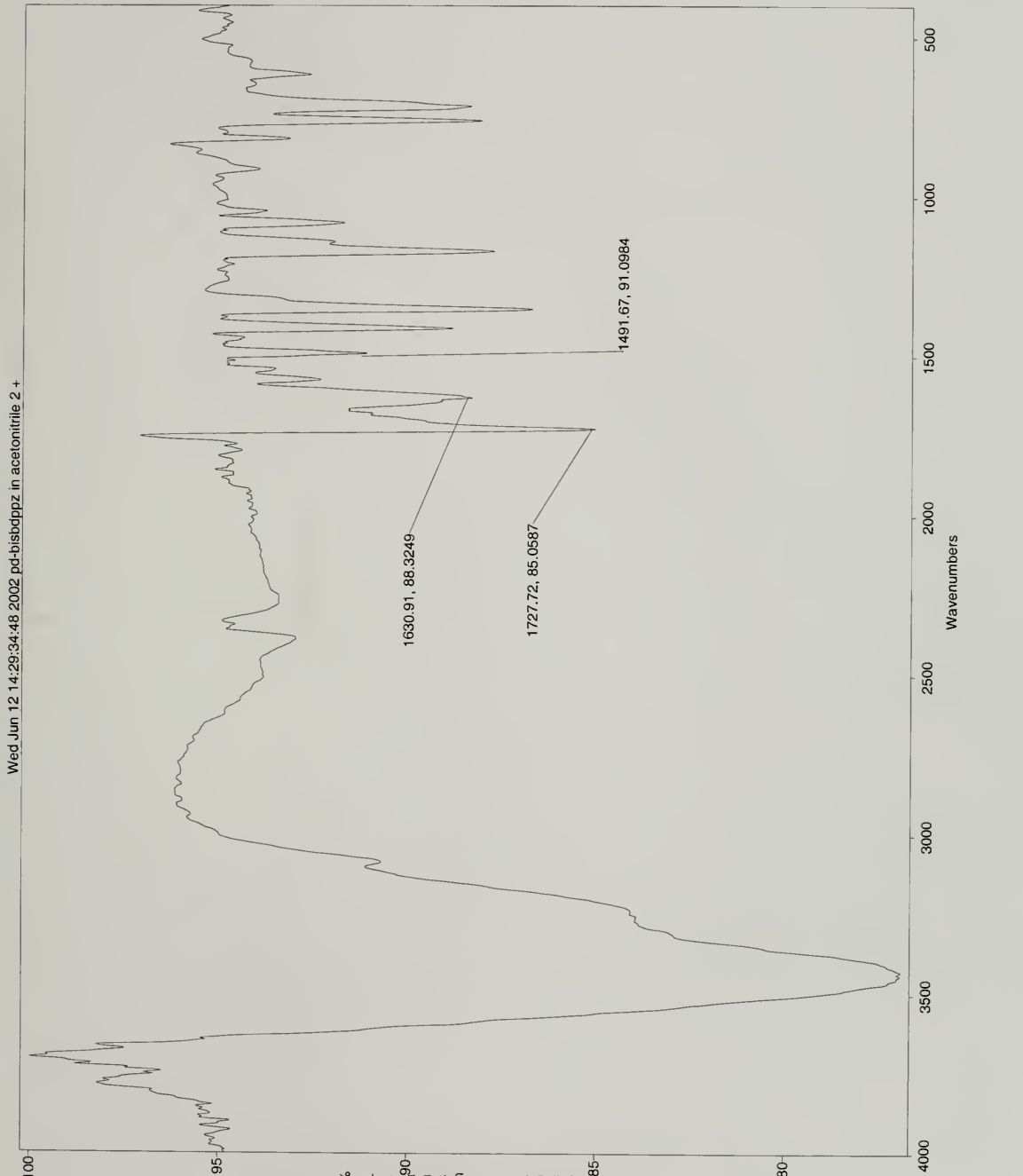
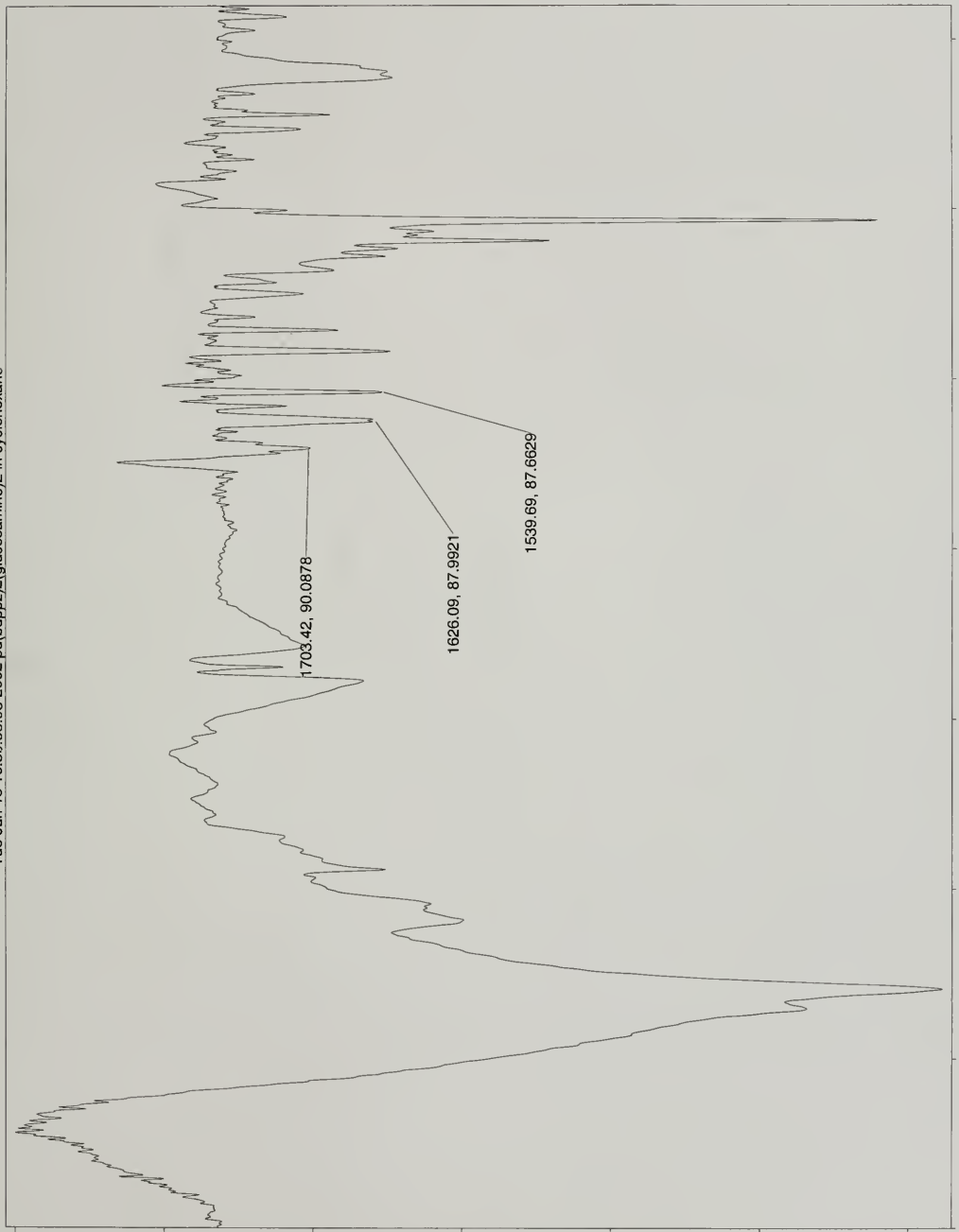


Figure A16: FT/IR of [Pd(bdppz-glucosamine)Cl2] A16



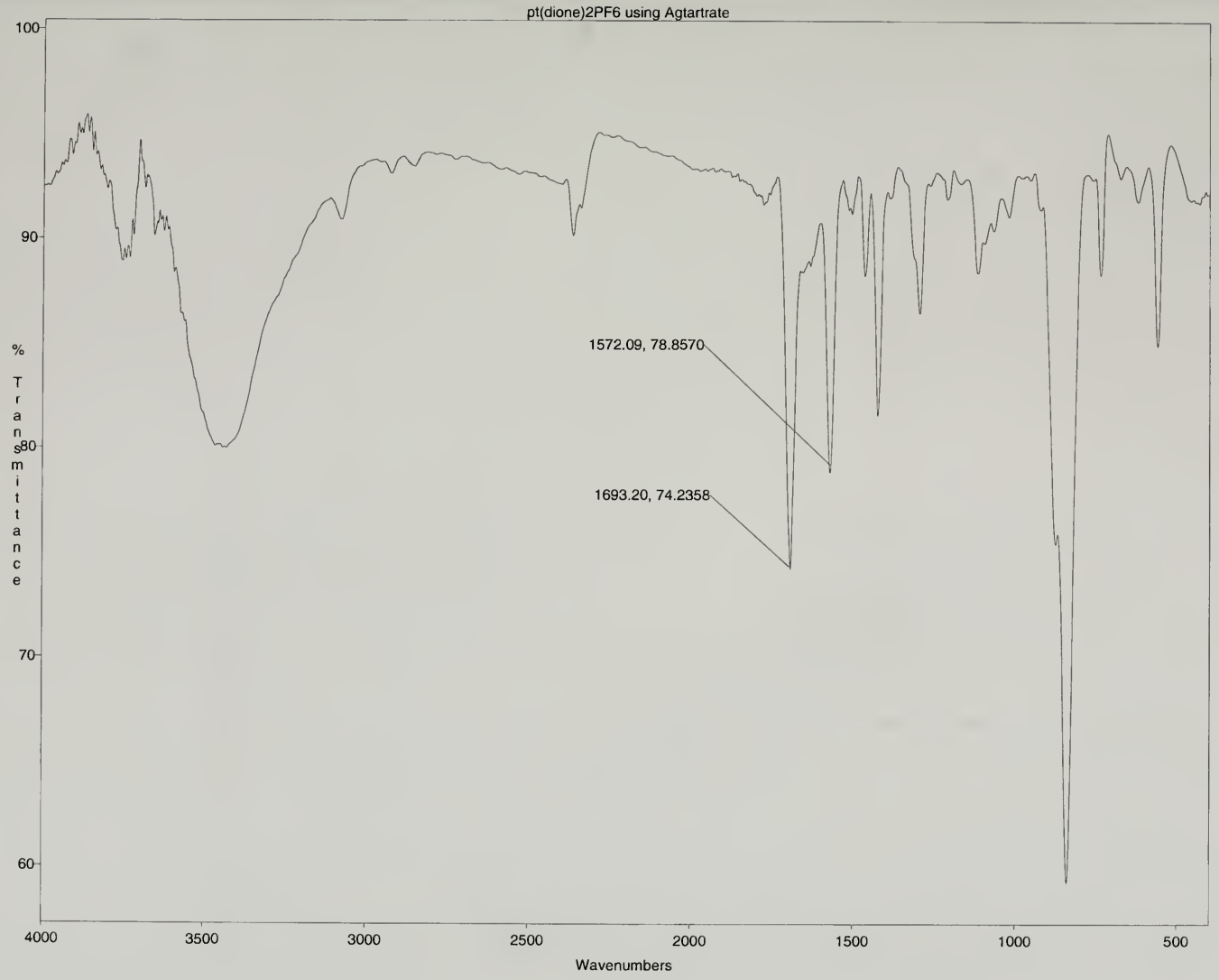


Figure A17: FT/IR of [Pt(dione)$_2$(PF$_6$)$_2$]

A17

Figure A18: FT/IR of $[Pt(dione)_2Cl_2]$

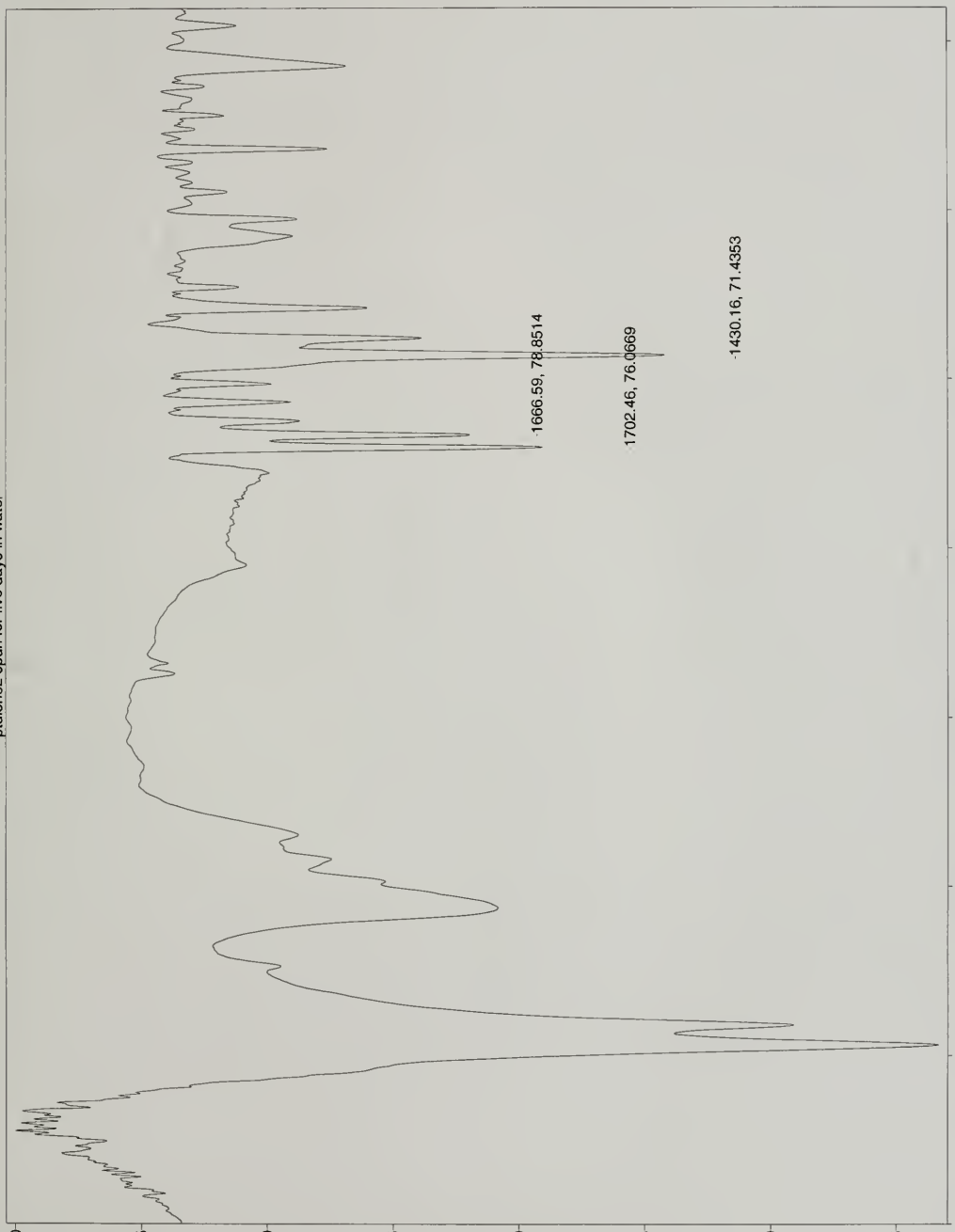
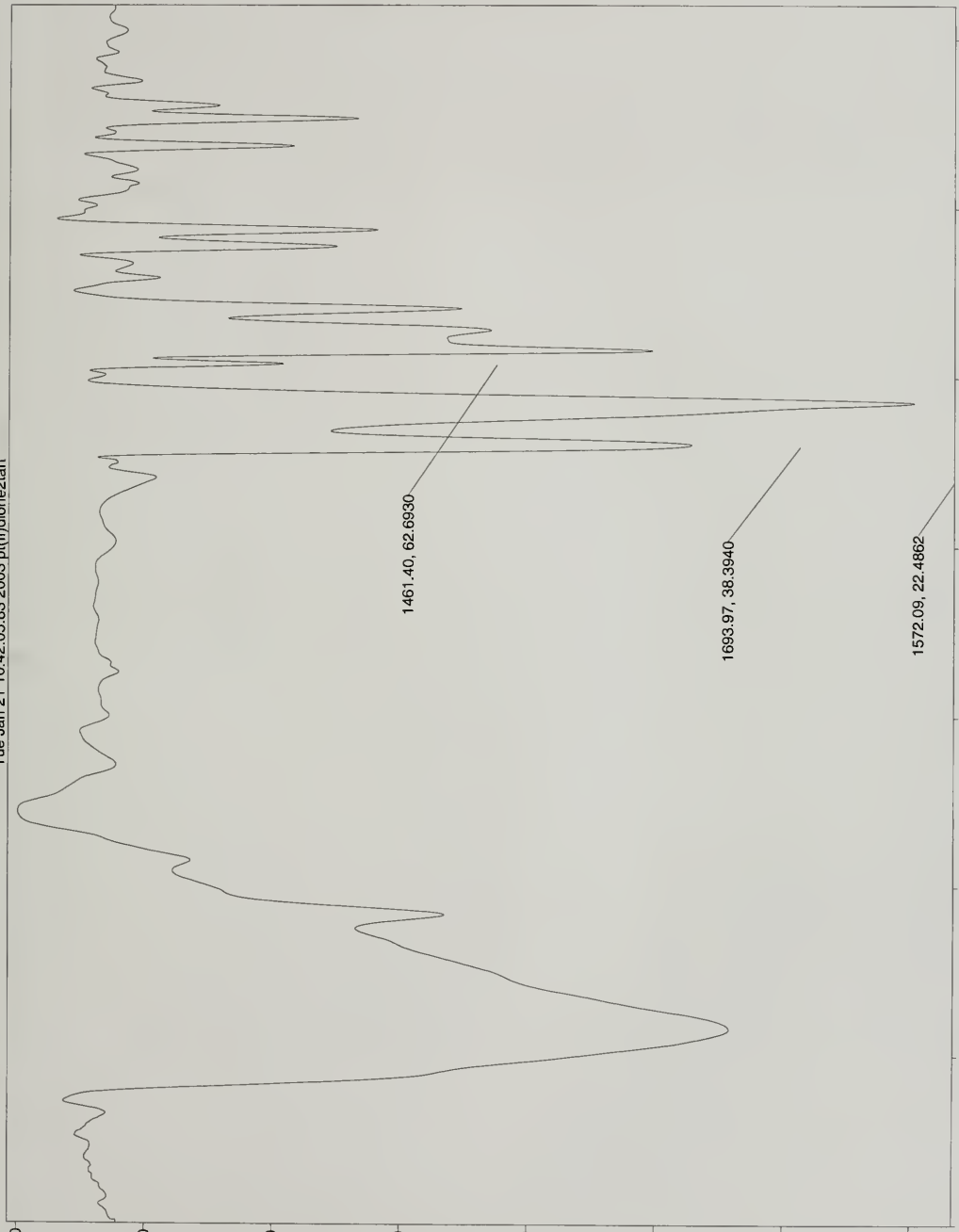


Figure A19: FT/IR of [Pt(dione)$_2$(Tartrate)]



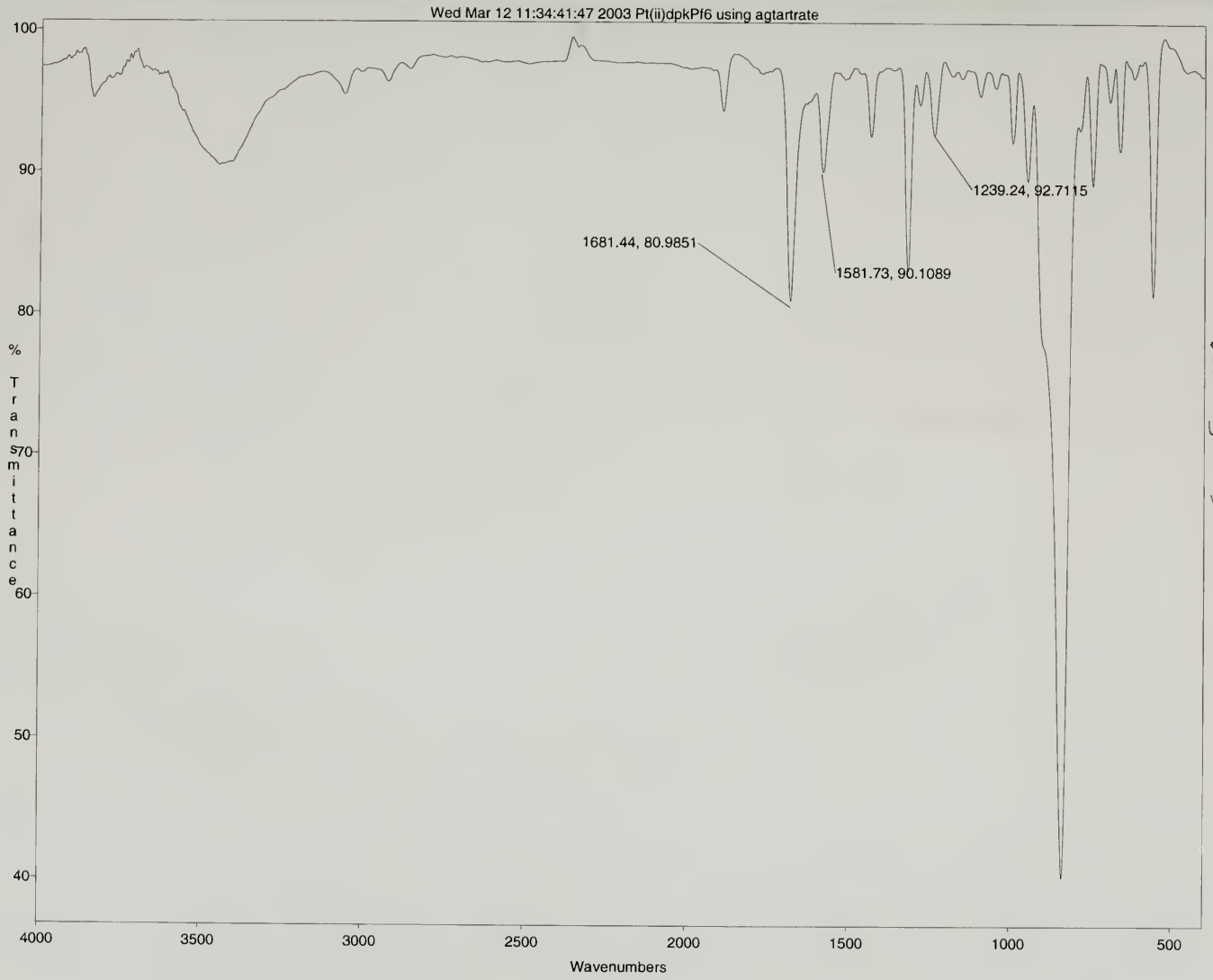


Figure A20: FT/IR of [Pt(dpk)2](PF6)2 using Ag2Tartrate

A20

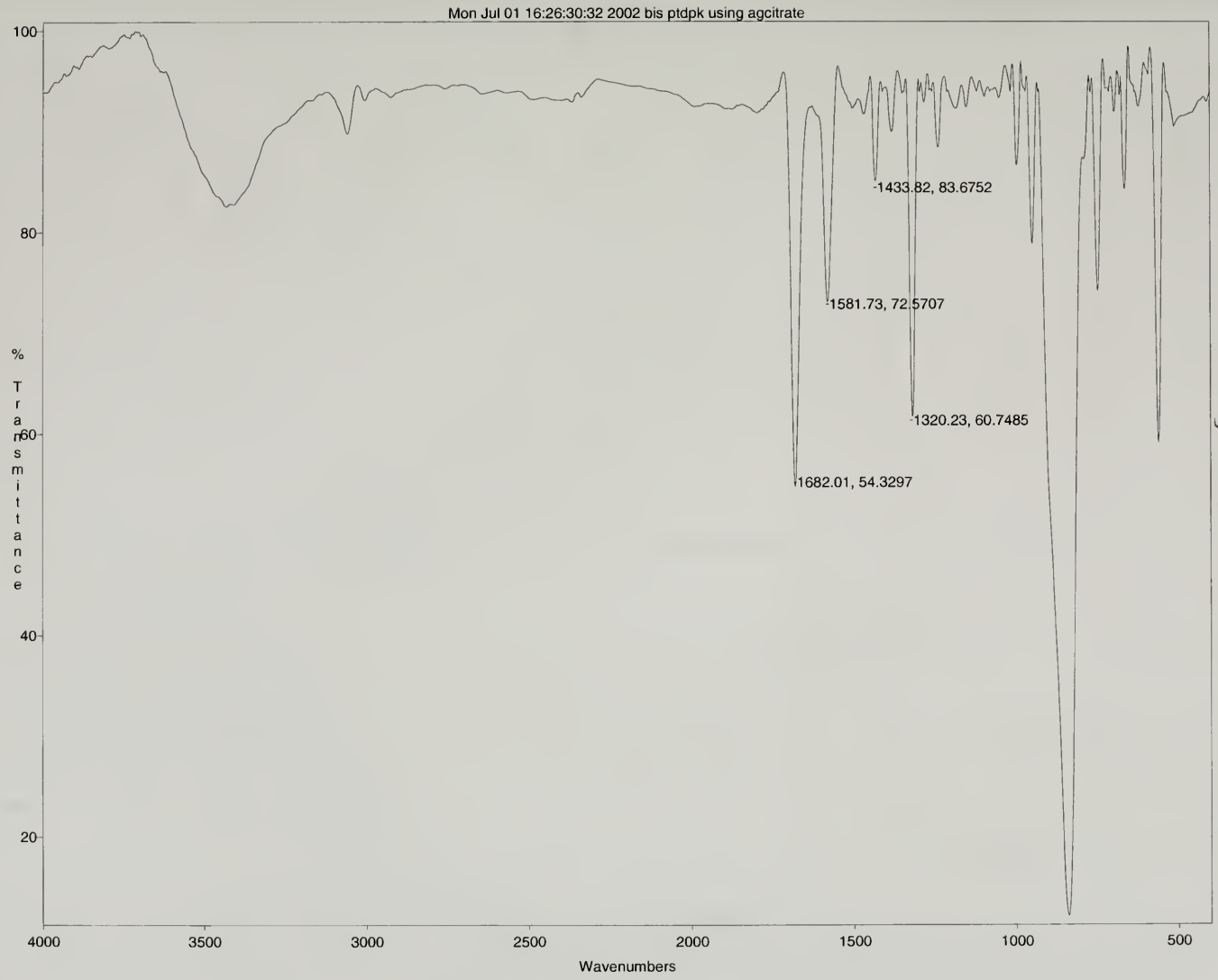


Figure A21: FT/IR of [Pt(dpk)2(PF6)2] using Ag3Citrate

A21

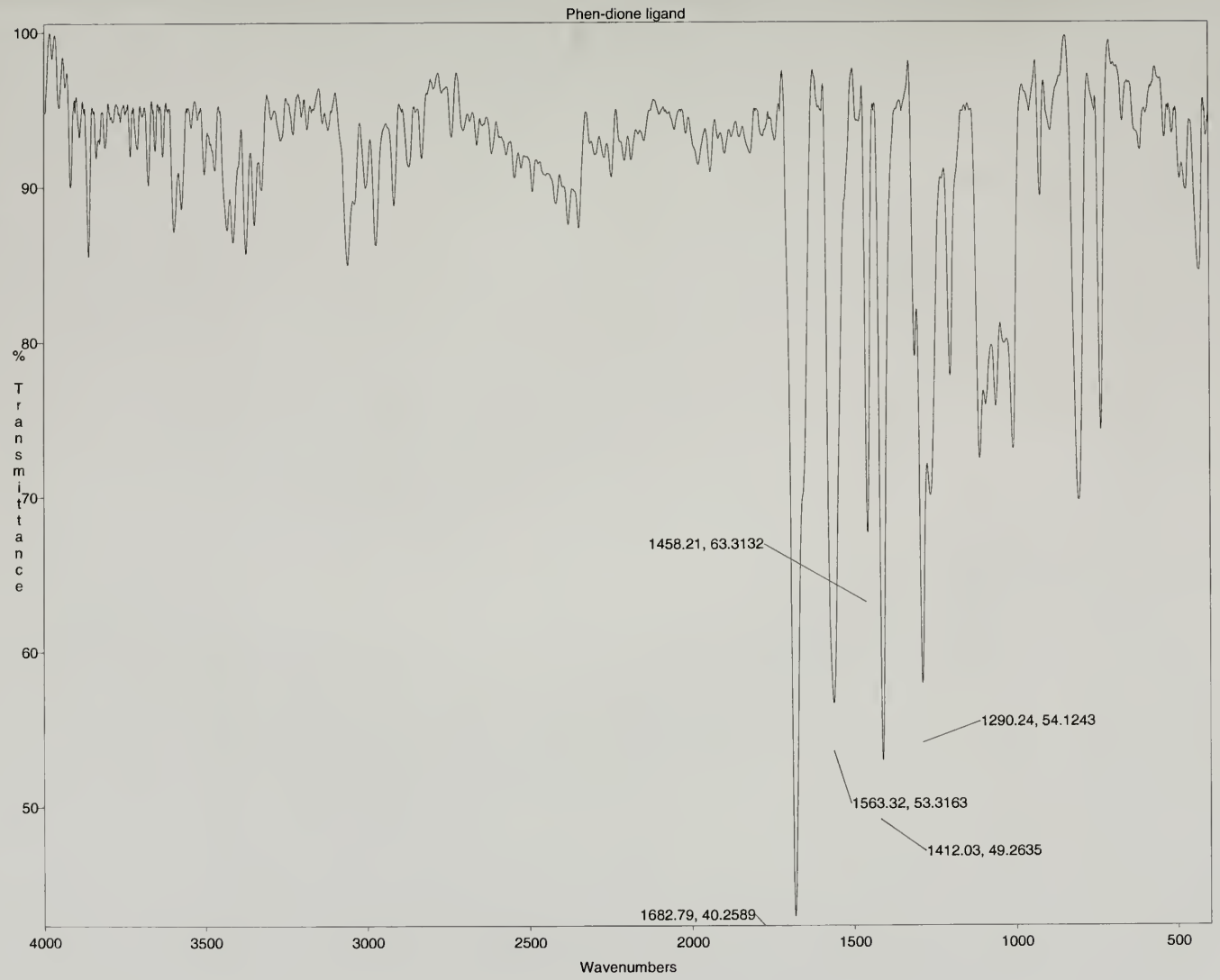


Figure A22: FT/IR of Dione

Figure A 23: FT/IR of glucose

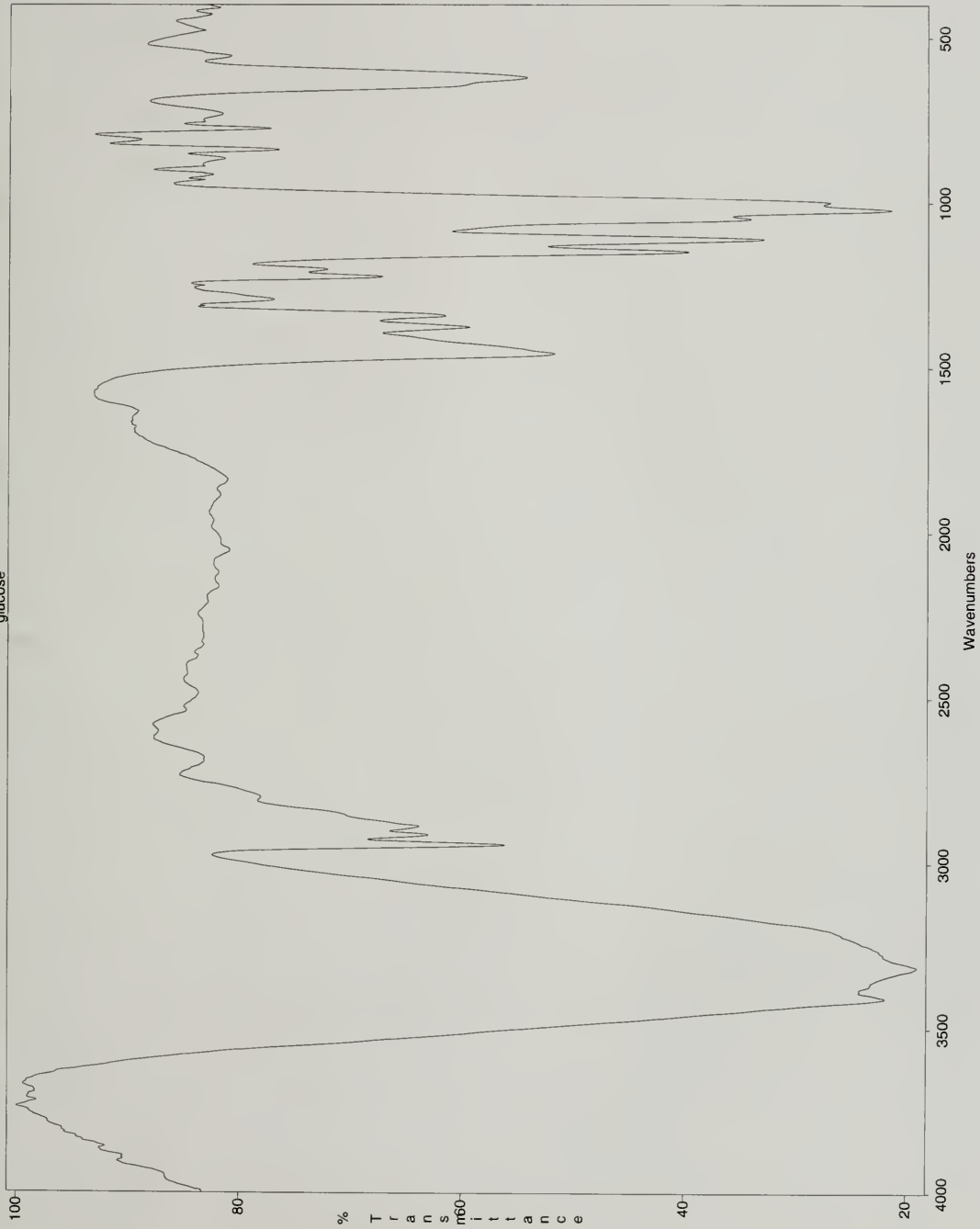


Figure A24: FT/IR of glucosamine

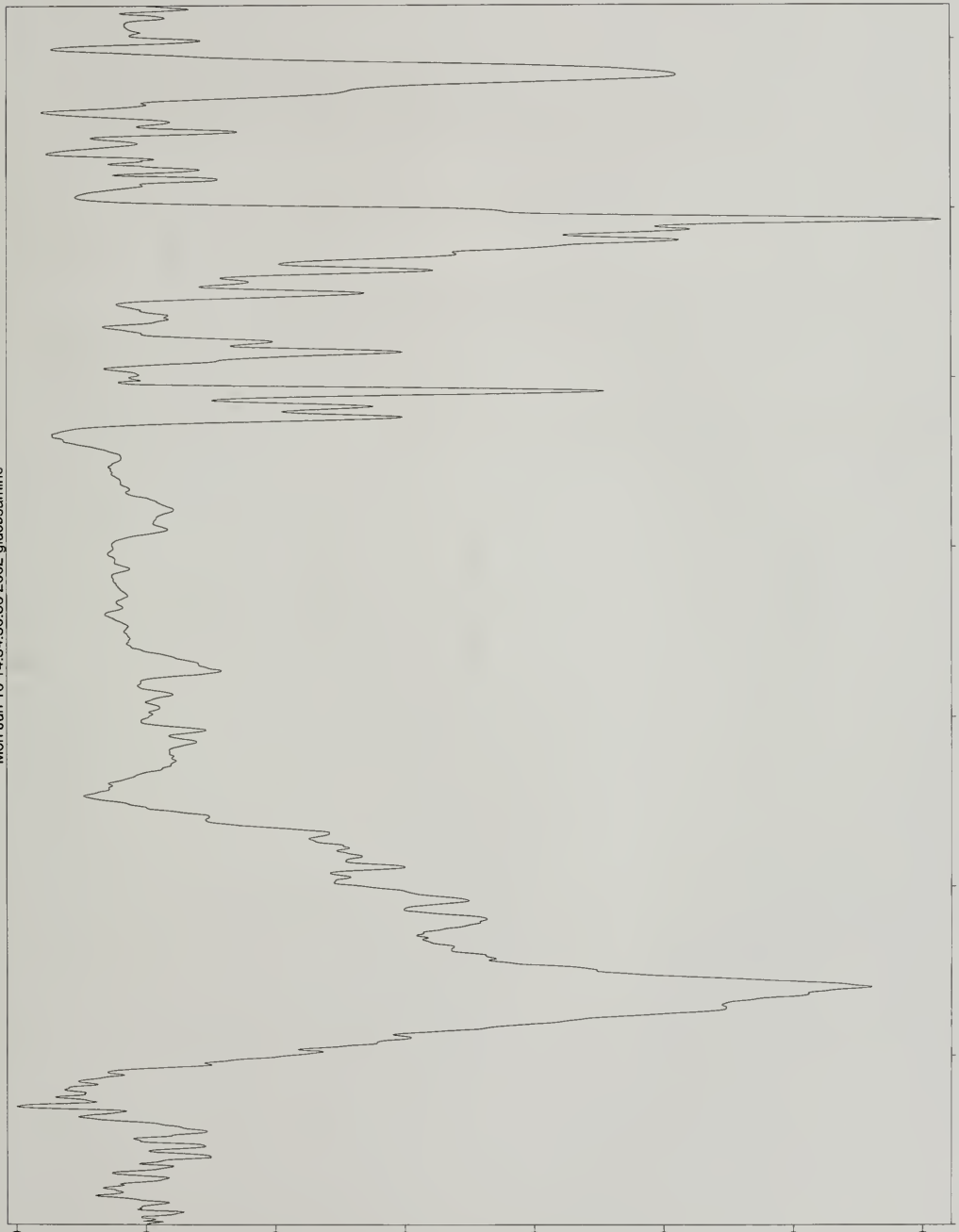


Figure A25: FT/IR of dpk

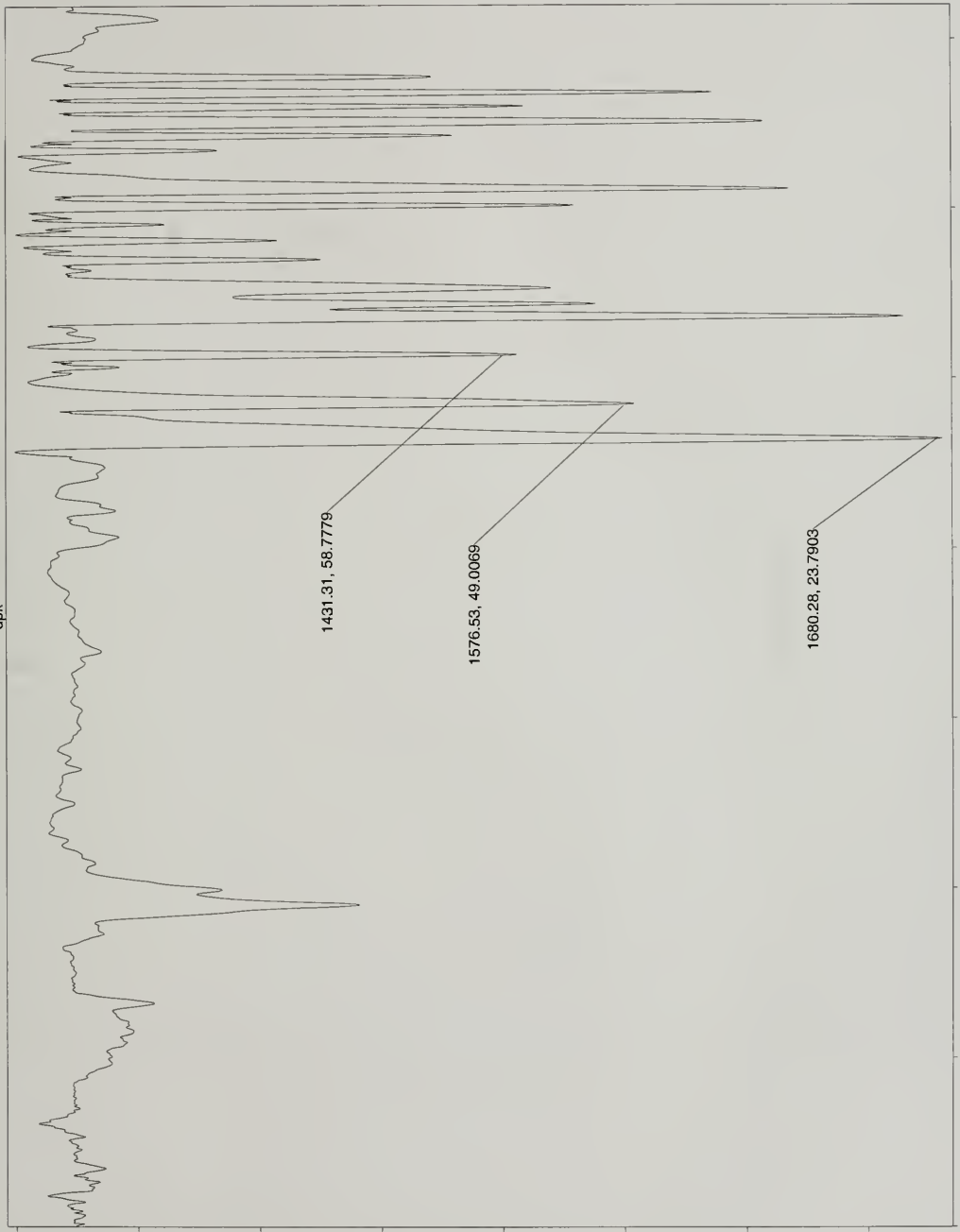
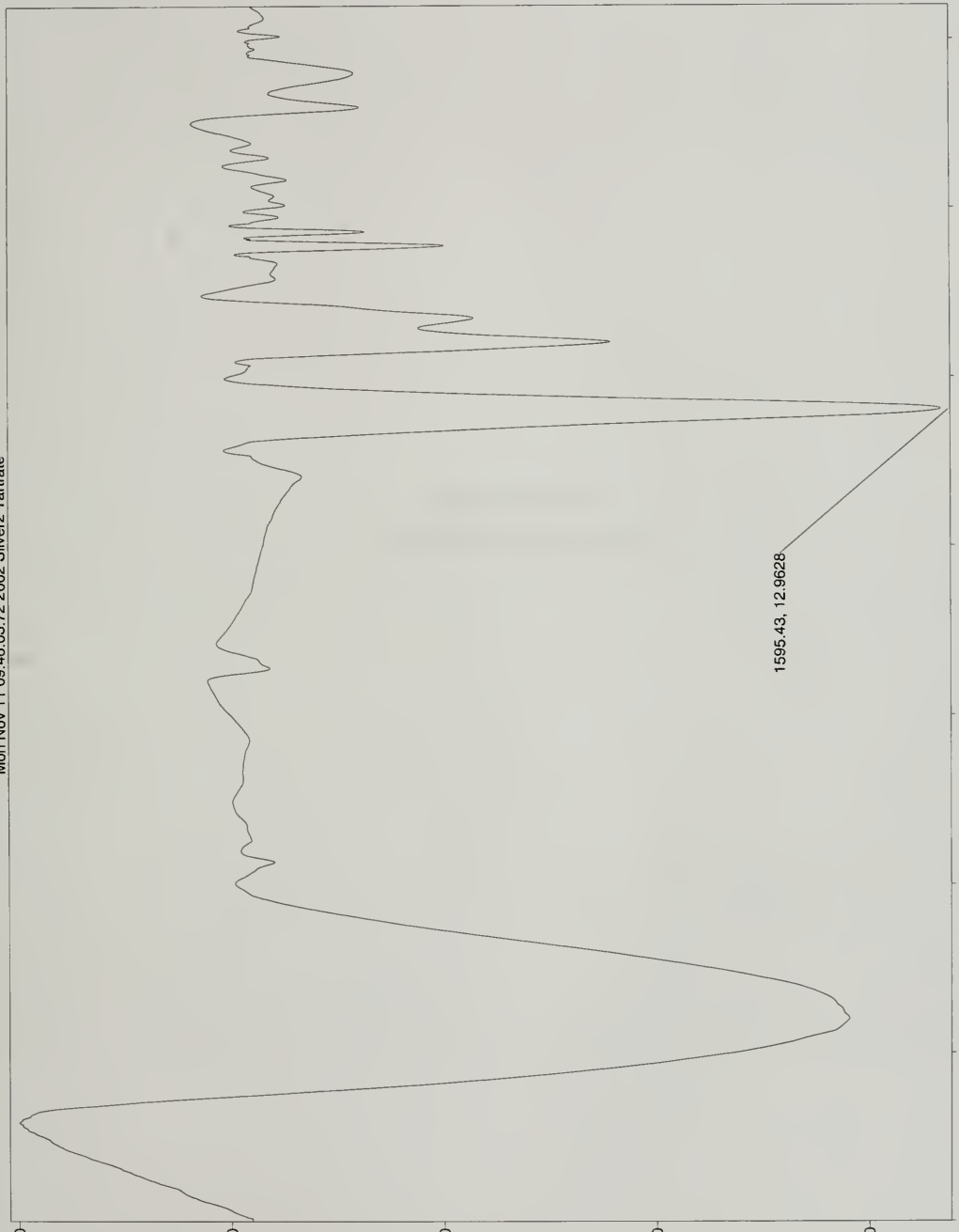


Figure A26: FT/IR of Ag_2 Tartrate



Appendix B
GC/MS Spectrum

Figure B1: GC/MS of bdppz

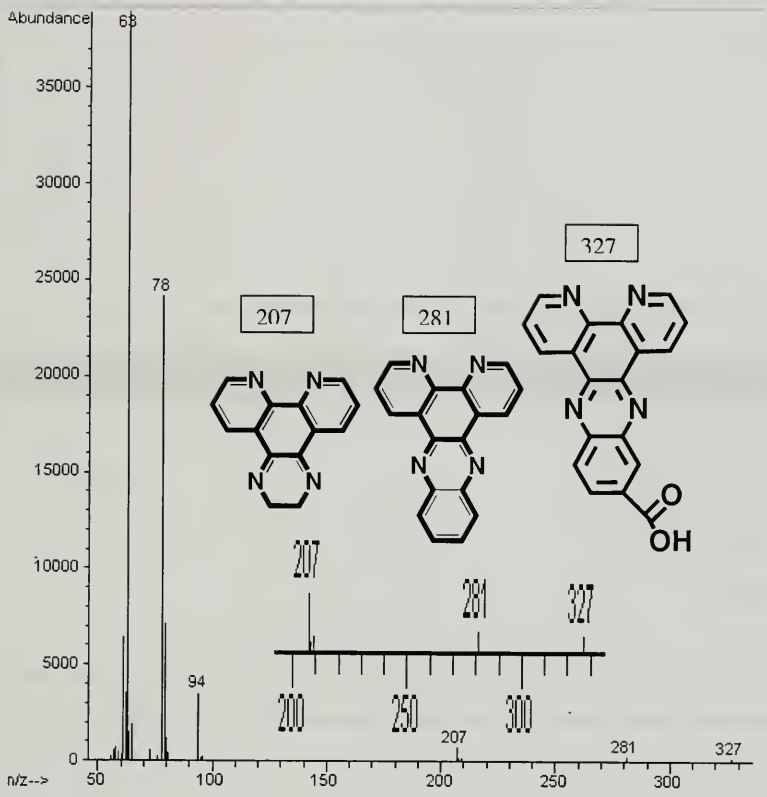
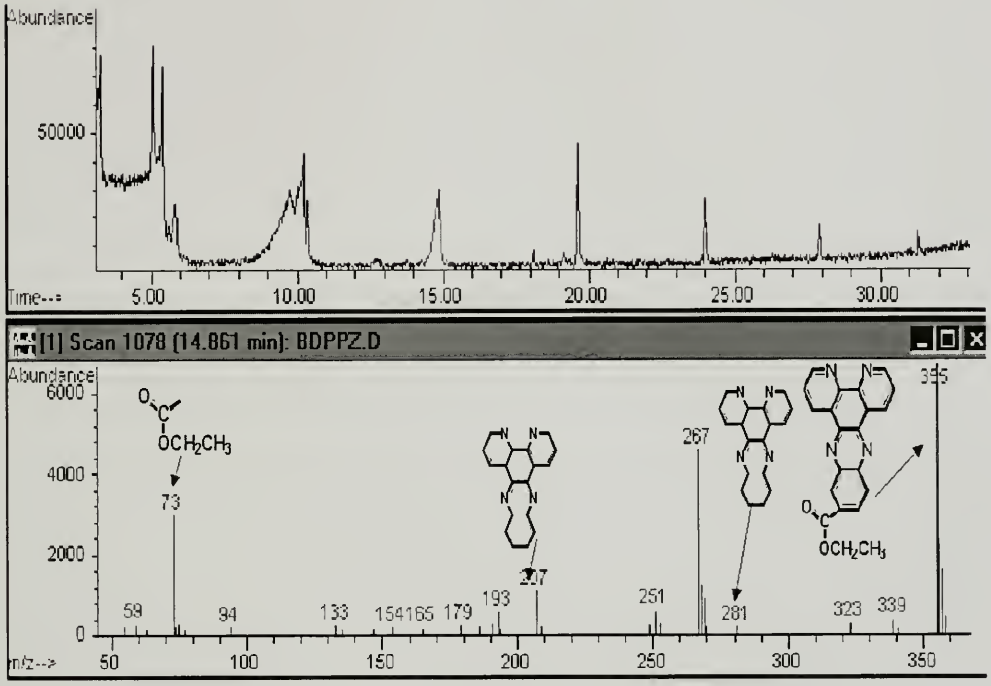
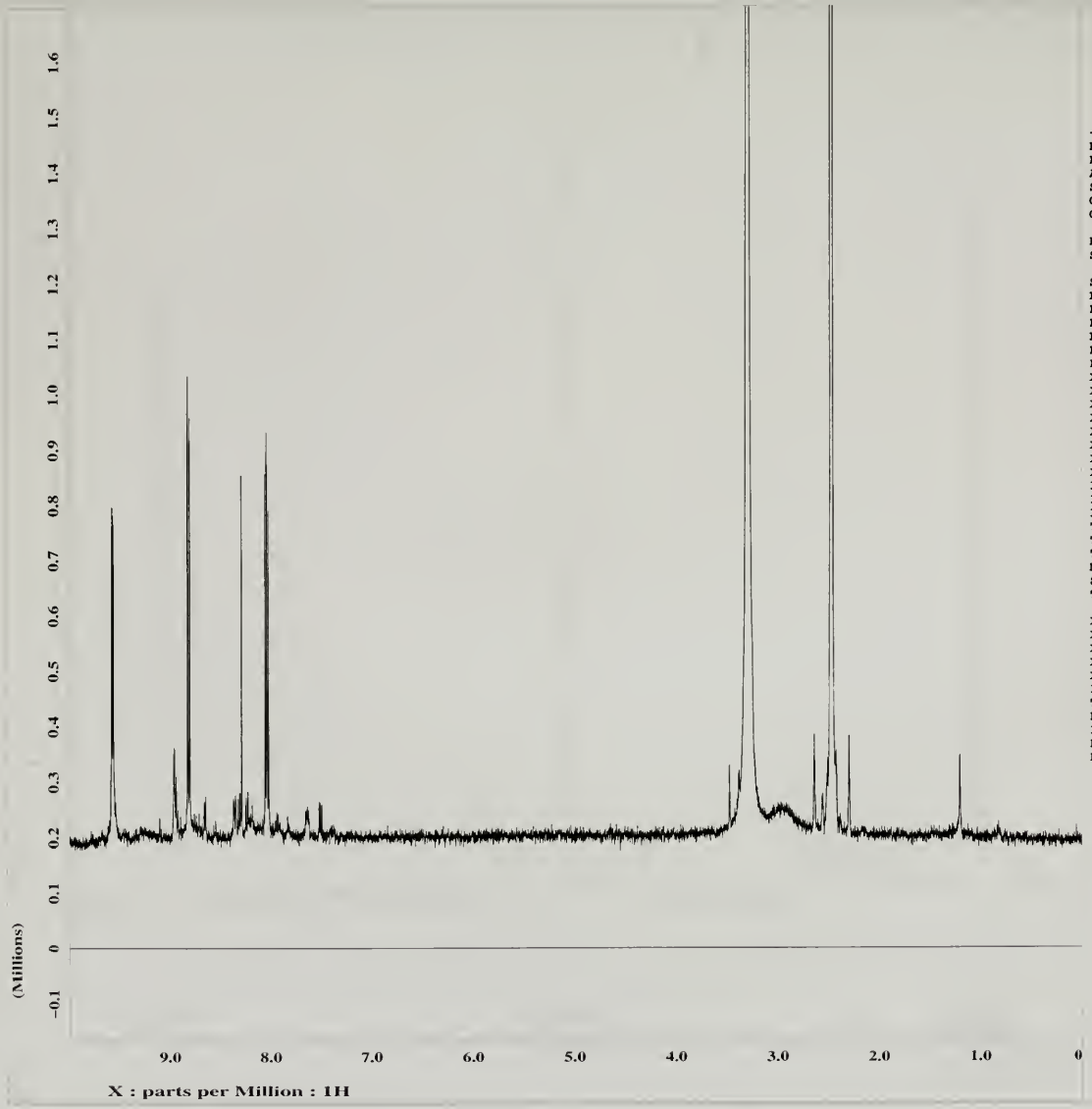


Figure B2: GC/MS of ethyl-bdppz (bappz in ethanol)



Appendix C
NMR Spectrum

Appendix C
NMR Spectrum



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Revision Date      = 11-FEB-2003 16:38:01
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Irr_offset         = 5[ppm]
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Tri_mode           = Off
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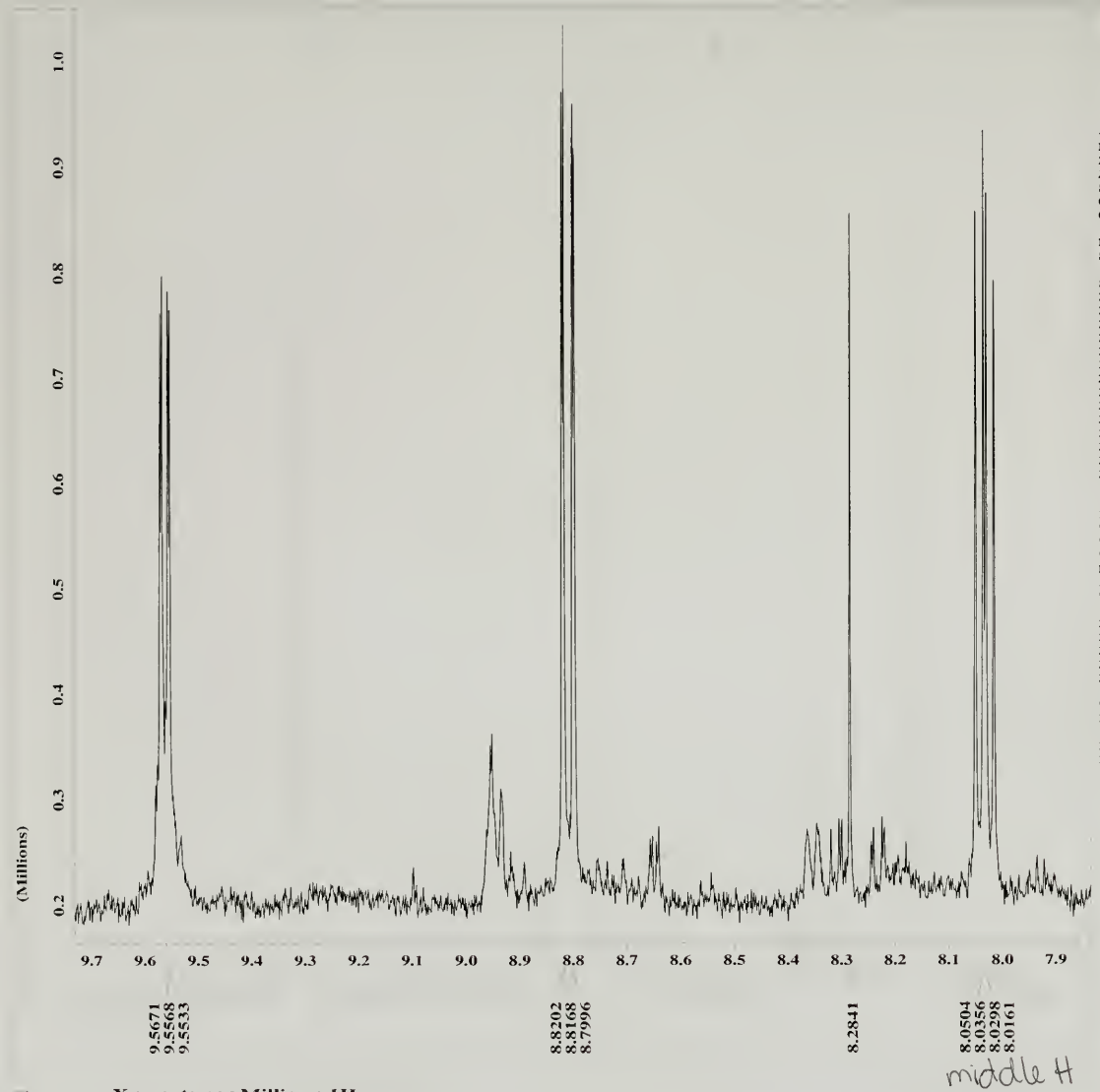
bring back & run 128 scans

Figure C1: 1H-NMR of [Pt(dione)Cl4]

C1



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X_pulse            = 6.6[us]
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Tri_mode           = Off
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what multiplicity do they have?

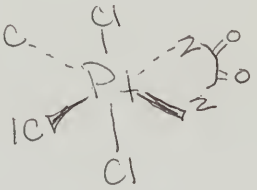
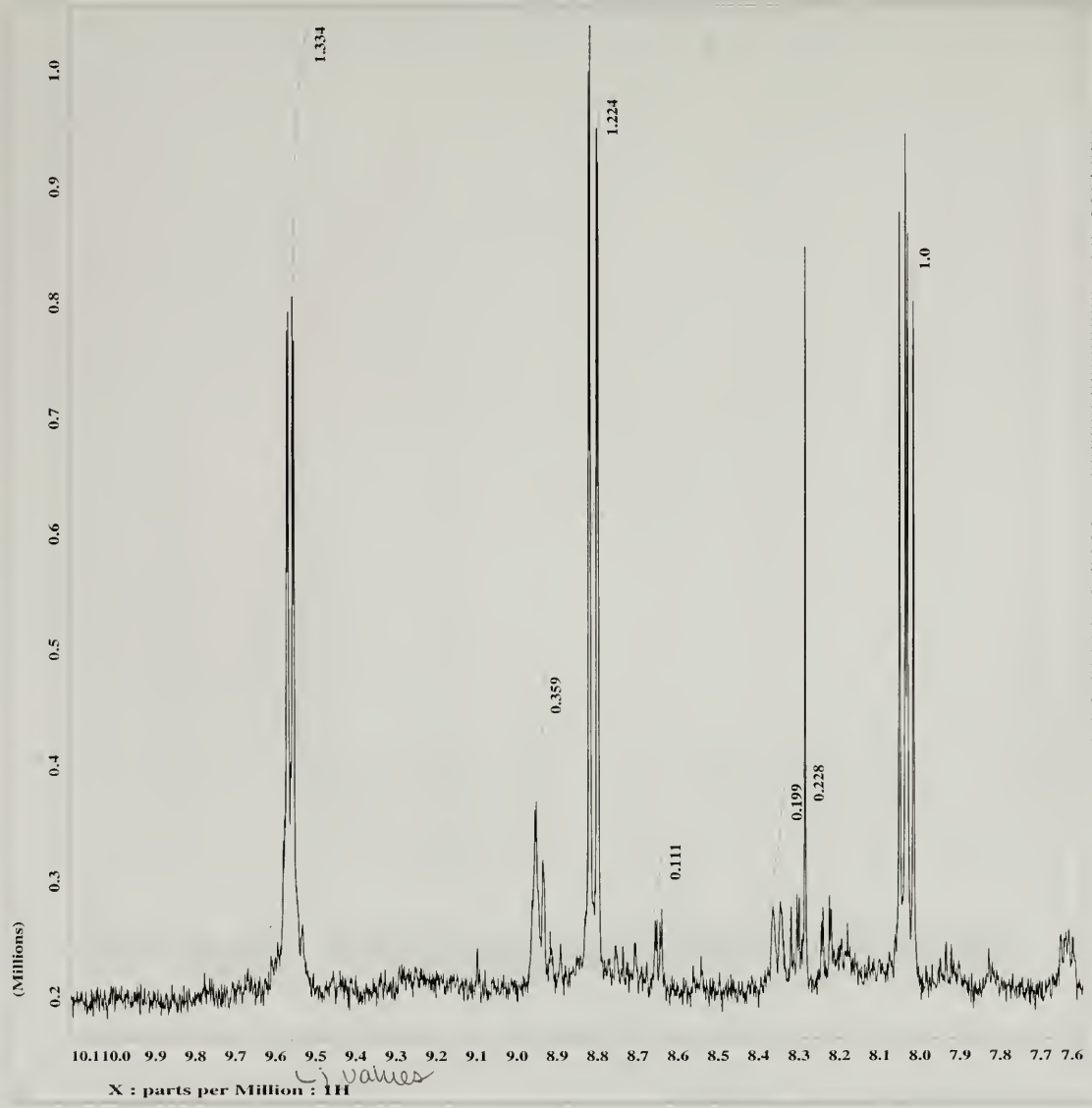


Figure C2: ^{1}H-NMR of Pt(dione)Cl$_4$

C2



JEOL

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Tri_offset         = 5[ppm]
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X_angle            = 45[deg]
X_atn              = 3[dB]
X_pulse            = 6.6[us]
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Tri_mode           = Off
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Relaxation_delay   = 5[s]
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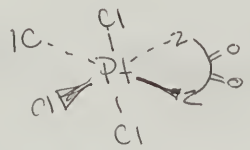


Figure C3: ^{1}H-NMR of [Pt(dione)Cl$_2$] integration

C3

C4

Figure C4: ^{1}H-NMR of [Pd(dione-glucosamine)Cl$_2$]

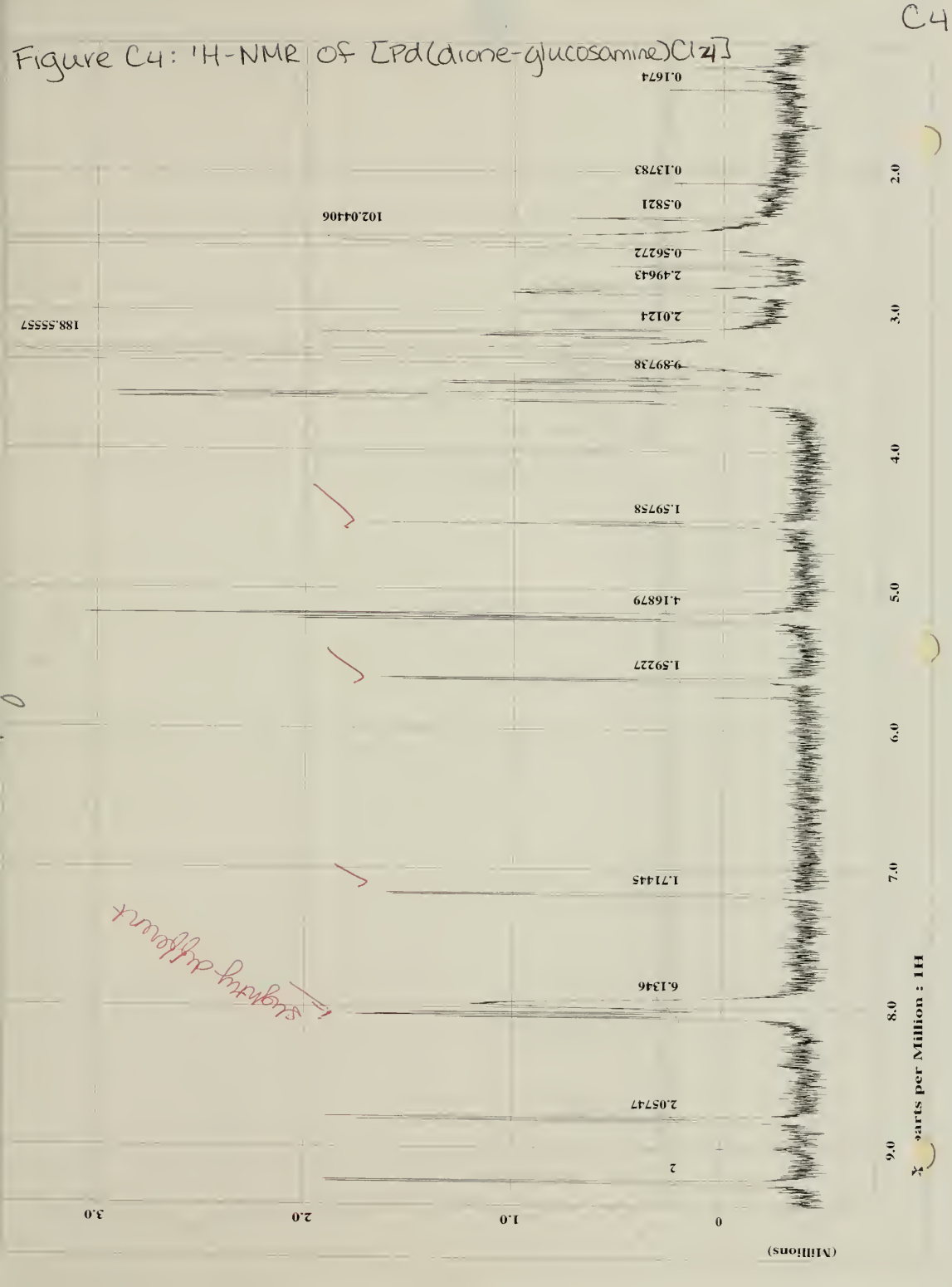
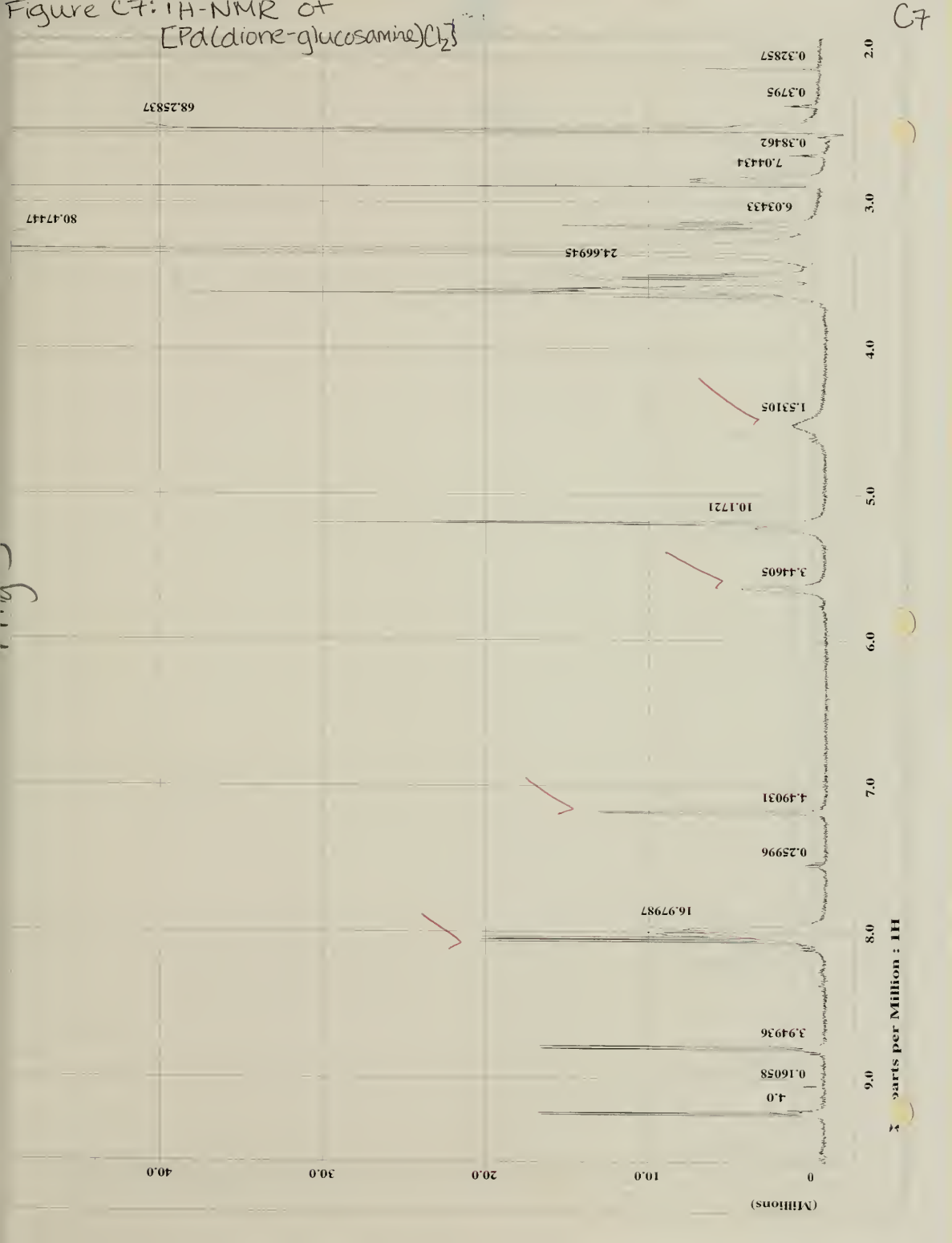


Figure C5: ^{1}H-NMR of [Pd(dione-glucosamine)Cl] w/ D_2O

Figure C6: ^{1}H-NMR of [Pd(dione)$_2$Cl$_2$]

Figure C7: 1H-NMR of [Pd(dione-glucosamine)Cl2]



C7

Figure C8: ^1H-NMR of [Pd(dione glucosamine)Cl$_2$] w/ D_2O

Figure C9: ^{1}H-NMR of [Pd(bdppz-glucosamine)Cl$_2$]

C9

Figure C10: ^{1}H-NMR of [Pd(bdppz-glucosamine)Cl$_2$] w/ D_2O

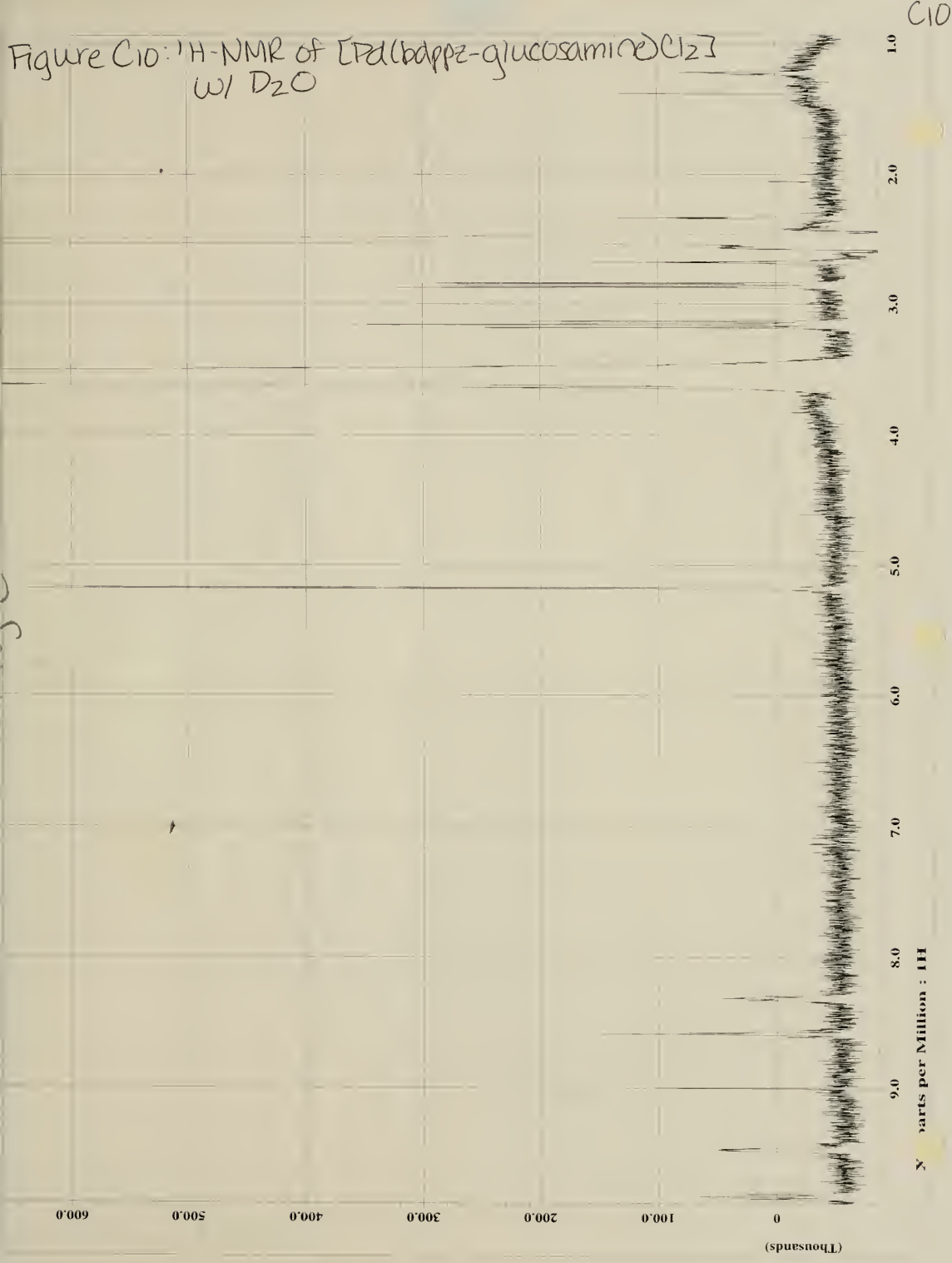


Figure C11: ^{1}H-NMR of [Pt(dione)$_2$ Tartrate]

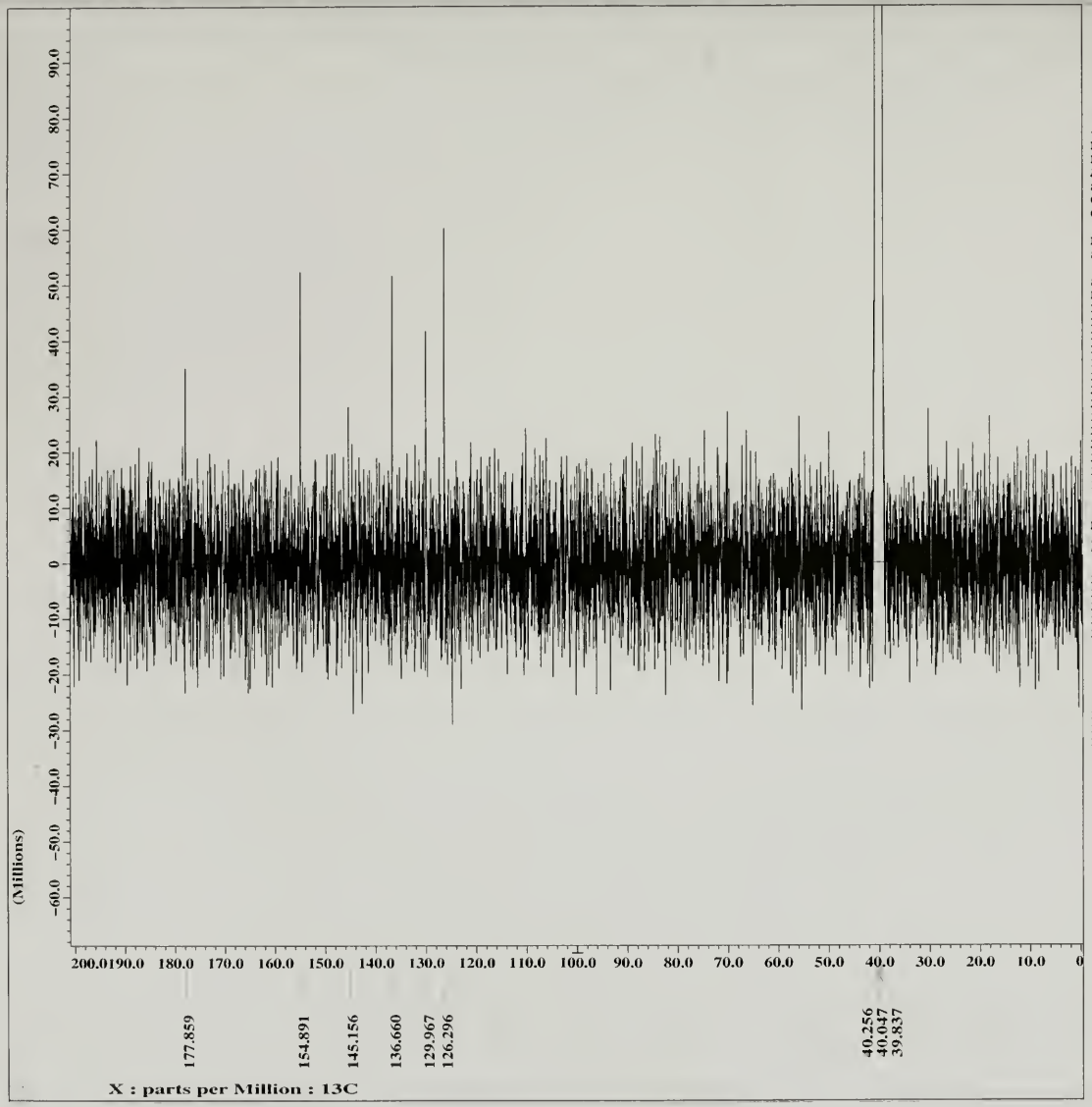


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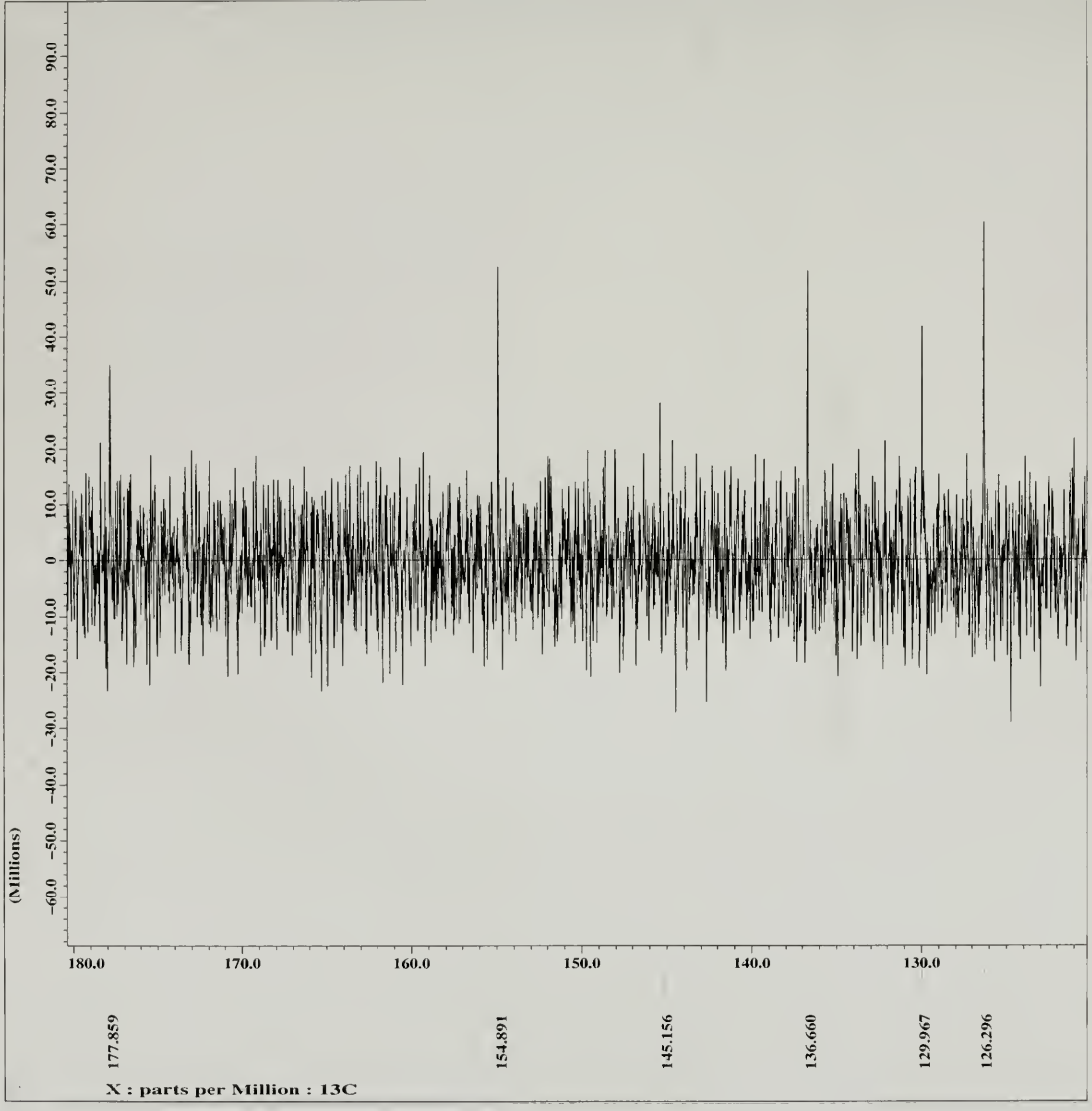
Figure C12: ^{13}C-NMR of Pt(dione)2tartrate

C12



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X_resolution       = 0.95846665[Hz]
X_sweep            = 31.40703518[kHz]
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Figure C13: 13C-NMR of [Pt(dione)$_2$Tartrate]

C13

Appendix D
X-Ray Crystallography

Appendix D
X-Ray Crystallography

APPENDIX D: Crystallographic data for [Pt(dione)Cl_2] & {[Pd(dpk)$_2$][PF_6]$_2$}$_n$ (polymer)

[Pt(dione)Cl_2]

Space Group and Cell Dimensions Monoclinic, C c
a 9.9445(11) b 22.906(3) c 7.5534(9)
beta 111.735(1)
Volume 1598.3(3)A**3

Empirical formula : Pt Cl2 C14 H12 N2 O3 S

Cell dimensions were obtained from 870 reflections with 2Theta angle
in the range 10.00 - 140.00 degrees.

Crystal dimensions : 0.10 X 0.07 X 0.03 mm

FW = 554.31 Z = 4 F(000) = 1037.18

Dcalc 2.304Mg.m-3, mu 20.24mm-1, lambda 1.5418A, 2Theta(max) 140.0

The intensity data were collected on a Bruker SMART 1K diffractometer,
using the omega scan mode.
The h,k,l ranges used during structure solution and refinement are :--
Hmin,max -12 10; Kmin,max -26 26; Lmin,max -9 8
No. of reflections measured 6530
No. of unique reflections 2268
No. of reflections with Inet > 2.5sigma(Inet) 2198
Merging R-value on intensities 0.028
Correction was made for absorption using SADABS
Ratio of minimum to maximum apparent transmission: 0.408232
Additional spherical absorption correction applied with mu*r = 0.6750

Details of the last least squares cycle
35 atoms, 207 parameters Full-matrix on Fo Counter wts (k 0.000500)
The residuals are as follows :--
Significant reflections: 2198 Rf 0.028, Rw 0.035
All reflections: 2268 Rf 0.029, Rw 0.036
Included reflections: 2198 Rf 0.028, Rw 0.035 GoF 1.1595
where Rf = Sum(Fo-Fc)/Sum(Fo),
Rw = Sqrt[Sum(w(Fo-Fc)**2)/Sum(wFo**2)] and
GoF = Sqrt[Sum(w(Fo-Fc)**2)/(No. of reflns - No. of params.)]
The maximum shift/sigma ratio was 0.000.

Last D-map: Minimum density -1.150e/A**3, Maximum density 1.110e/A**3.

Secondary ext. coeff. 0.2207microns sigma 0.0257

The following references are relevant to the NRCVAX System.

1. Full System Reference :
Gabe, E.J., Le Page, Y., Charland,.J.-P., Lee, F.L. and White, P.S. (1989) J. Appl. Cryst., 22, 384-387.

2. Scattering Factors from Int. Tab. Vol. 4 :
International Tables for X-ray Crystallography, Vol. IV, (1974) Kynoch Press, Birmingham, England.

The following references may also be relevant.

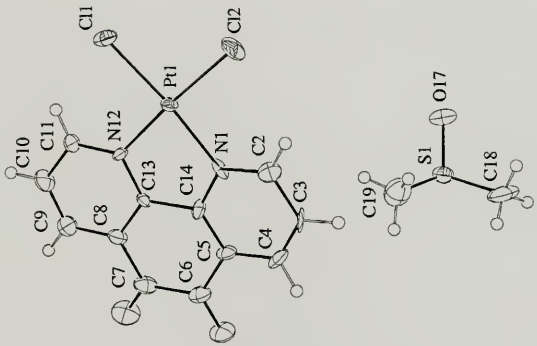
3. ORTEP Plotting :
Johnson, C.K., (1976) ORTEP - A Fortran Thermal Ellipsoid Plot Program, Technical Report ORNL-5138, Oak Ridge

4. Pluto Plotting :
S. Motherwell, University Chemical Laboratory, Cambridge, 1978

5. Missing Symmetry Treatment by MISSYM :
Le Page, Y., (1988) J. Appl. Cryst., 21, 983-984.

6. Grouping of Equivalent Reflections in DATRD2 :
Le Page, Y. and Gabe, E.J., (1979) J. Appl. Cryst., 12, 464-466.

7. Extinction Treatment :
Larson, A.C., (1970) p.293, Crystallographic Computing, Munksgaard, Copenhagen.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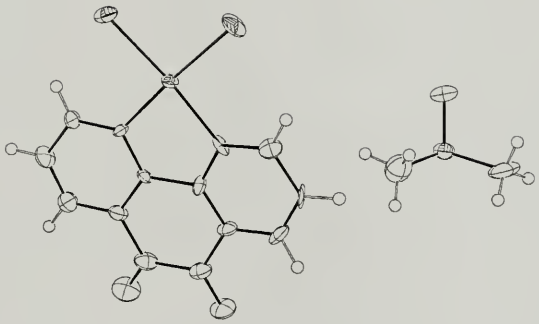
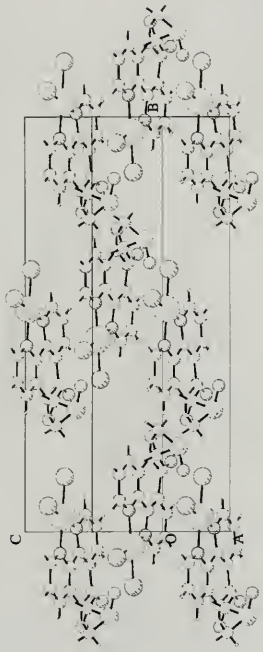
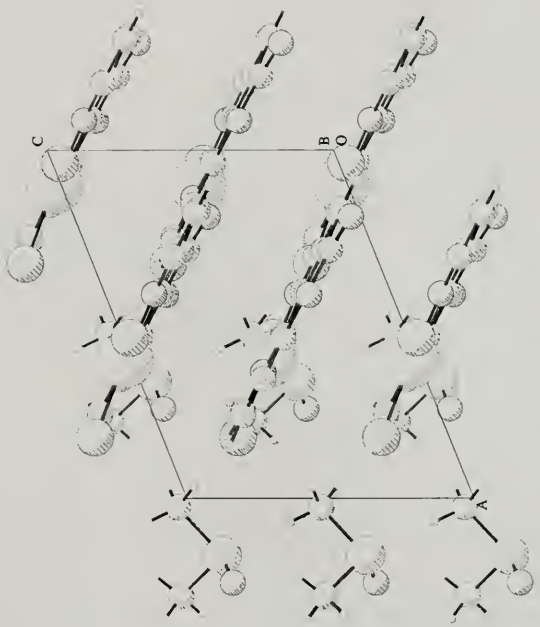
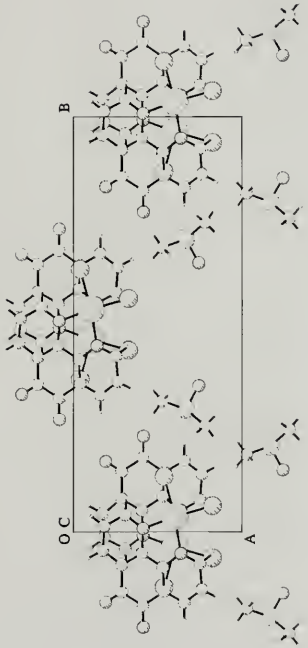
Cl2
Pt1
N12
N1
C2
C3
C4
C5
C6
C7
C8
C9
C10
C11
C13
C14
S1
O17
C18
C19




B
C


C
B
O
A


B
O C
A

28-Mar-2003

Table . Atomic Parameters x,y,z and Biso.
E.S.Ds. refer to the last digit printed.

	x	y	z	Biso
Pt1	0.10164	0.536399(12)	0.02238	1.386(17)
C11	0.0380 (3)	0.63287 (10)	-0.0251 (4)	2.34 (9)
C12	0.3253 (3)	0.56246 (14)	0.2360 (4)	3.11 (11)
N1	0.1375 (7)	0.4483 (4)	0.0569 (10)	1.5 (4)
C2	0.2513 (15)	0.4239 (5)	0.1820 (17)	2.2 (5)
C3	0.2621 (10)	0.3614 (5)	0.1886 (15)	2.2 (4)
C4	0.1576 (12)	0.3294 (5)	0.0672 (17)	2.3 (5)
C5	0.0385 (12)	0.3570 (4)	-0.0603 (15)	1.7 (4)
C6	-0.0871 (11)	0.3222 (4)	-0.2036 (15)	2.2 (5)
C7	-0.2138 (11)	0.3550 (4)	-0.3474 (14)	2.3 (4)
C8	-0.2134 (10)	0.4209 (4)	-0.3271 (14)	1.8 (4)
C9	-0.3268 (13)	0.4554 (5)	-0.4419 (17)	2.6 (5)
C10	-0.3178 (11)	0.5140 (5)	-0.4269 (16)	2.7 (4)
C11	-0.1929 (12)	0.5409 (4)	-0.2870 (15)	1.9 (4)
N12	-0.0869 (8)	0.5083 (3)	-0.1710 (11)	1.3 (3)
C13	-0.0937 (10)	0.4485 (4)	-0.1945 (13)	1.3 (4)
C14	0.0299 (13)	0.4151 (4)	-0.0650 (16)	1.6 (4)
O15	-0.0851 (9)	0.2703 (3)	-0.2117 (12)	3.0 (4)
O16	-0.3085 (9)	0.3311 (4)	-0.4668 (11)	3.4 (4)
S1	0.6650 (3)	0.29479 (12)	-0.0437 (4)	2.24 (11)
O17	0.7427 (9)	0.3517 (3)	-0.0424 (10)	2.7 (3)
C18	0.7810 (17)	0.2552 (5)	0.1567 (20)	4.0 (6)
C19	0.5272 (18)	0.3150 (7)	0.0446 (23)	4.1 (7)
H2	0.326	0.448	0.271	3.1
H3	0.348	0.343	0.275	2.8
H4	0.159	0.288	0.074	3.4
H9	-0.412	0.438	-0.532	3.2
H10	-0.394	0.538	-0.512	3.2
H11	-0.185	0.583	-0.278	2.4
H18a	0.833	0.227	0.113	4.6
H18b	0.724	0.236	0.218	4.6
H18c	0.846	0.282	0.245	4.6
H19a	0.470	0.282	0.048	5.1
H19b	0.466	0.344	-0.041	5.1
H19c	0.569	0.332	0.170	5.1

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid

Table of u(i,j) or U values *100.
E.S.Ds. refer to the last digit printed

	u11(U)	u22	u33	u12	u13	u23
Pt1	1.664(18)	1.524(17)	1.993(19)	-0.431(22)	0.577(13)	-0.369(22)
C11	3.80 (12)	1.58 (10)	3.71 (13)	-0.44 (9)	1.61 (10)	-0.23 (9)
C12	2.04 (12)	4.50 (16)	4.04 (15)	-1.17 (12)	-0.33 (11)	-1.15 (13)
N1	0.9 (5)	3.6 (5)	0.5 (4)	-0.5 (3)	-0.5 (4)	-0.5 (3)
C2	3.6 (7)	2.3 (6)	2.6 (6)	-0.2 (5)	1.2 (6)	-0.7 (5)
C3	1.4 (5)	3.2 (6)	3.1 (5)	1.7 (4)	0.1 (4)	1.5 (5)
C4	4.0 (5)	1.5 (5)	4.6 (7)	1.3 (4)	3.2 (6)	1.3 (5)
C5	2.8 (6)	1.1 (5)	3.0 (5)	-0.3 (4)	1.6 (5)	-0.5 (4)
C6	3.7 (6)	1.8 (6)	3.3 (5)	-0.3 (4)	1.8 (5)	-0.3 (4)
C7	3.2 (5)	2.9 (5)	2.3 (5)	-1.1 (4)	0.6 (4)	-0.5 (4)
C8	2.1 (4)	2.2 (5)	2.6 (5)	-0.7 (4)	0.8 (4)	-0.1 (4)
C9	2.4 (6)	3.0 (6)	3.7 (6)	-0.2 (4)	0.3 (4)	0.2 (4)
C10	2.0 (6)	4.1 (6)	3.0 (5)	-0.2 (5)	-0.5 (4)	1.0 (5)
C11	1.6 (5)	2.4 (5)	2.3 (5)	0.0 (4)	-0.3 (4)	0.1 (4)
N12	2.0 (4)	0.8 (3)	2.3 (4)	0.1 (3)	1.0 (3)	0.2 (3)
C13	1.0 (4)	1.9 (5)	1.7 (5)	-0.4 (4)	0.1 (4)	0.0 (3)
C14	2.1 (5)	1.7 (5)	2.1 (5)	0.9 (4)	0.7 (4)	-0.1 (4)
O15	4.7 (5)	2.0 (4)	4.9 (5)	-0.4 (3)	2.3 (4)	-1.3 (3)
O16	5.2 (5)	4.3 (5)	3.4 (4)	-1.2 (4)	1.4 (4)	-1.8 (4)
S1	2.83 (12)	2.43 (14)	3.29 (14)	-0.62 (10)	1.16 (11)	-0.14 (10)
O17	5.0 (4)	2.1 (3)	3.8 (4)	-1.0 (3)	2.4 (4)	-0.3 (3)
C18	7.1 (9)	2.0 (5)	5.5 (8)	-1.6 (6)	1.6 (7)	0.3 (5)
C19	5.7 (9)	5.2 (10)	5.5 (9)	0.8 (7)	2.9 (7)	1.4 (7)
H2	3.9					
H3	3.6					
H4	4.3					
H9	4.1					
H10	4.0					
H11	3.1					
H18a	5.9					
H18b	5.9					
H18c	5.9					
H19a	6.5					
H19b	6.5					
H19c	6.5					

Anisotropic Temperature Factors are of the form
Temp=-2*Pi*Pi*(h*h*u11*astar*astar+---+2*h*k*u12*astar*bstar+---)

DISANG -- The NRCVAX Distance and Angle Program

The Space Group is C C NonCentrosymmetric
The Equivalent Positions are:
1) x y z 2) x -y 1/2+z

The Lattice is C-centred. The Centering Vectors are:
1) 0, 0, 0 2) 1/2, 1/2, 0

Pt(1)-Cl(1)	2.2900(24)	C(6)-O(15)	1.191(12)
Pt(1)-Cl(2)	2.291(3)	C(7)-C(8)	1.518(14)
Pt(1)-N(1)	2.049(10)	C(7)-O(16)	1.172(13)
Pt(1)-N(12)	2.009(8)	C(8)-C(9)	1.386(15)
Pt(1)-C(13)	2.855(9)	C(8)-C(13)	1.392(13)
Pt(1)-C(14)	2.884(11)	C(9)-C(10)	1.348(16)
N(1)-C(2)	1.302(15)	C(10)-C(11)	1.437(16)
N(1)-C(14)	1.356(14)	C(11)-N(12)	1.324(13)
C(2)-C(3)	1.436(16)	N(12)-C(13)	1.378(12)
C(3)-C(4)	1.323(17)	C(13)-C(14)	1.471(15)
C(4)-C(5)	1.373(16)	S(1)-O(17)	1.515(7)
C(5)-C(6)	1.539(15)	S(1)-C(18)	1.775(14)
C(5)-C(14)	1.332(14)	S(1)-C(19)	1.792(16)
C(6)-C(7)	1.522(15)		

Cl(1)-Pt(1)-Cl(2)	89.93(11)	C(6)-C(7)-C(8)	116.6(8)
Cl(1)-Pt(1)-N(1)	174.41(20)	C(6)-C(7)-O(16)	122.4(10)
Cl(1)-Pt(1)-N(12)	93.80(21)	C(8)-C(7)-O(16)	121.0(10)
Cl(1)-Pt(1)-C(13)	120.05(22)	C(7)-C(8)-C(9)	122.2(9)
Cl(1)-Pt(1)-C(14)	149.69(24)	C(7)-C(8)-C(13)	119.6(9)
Cl(2)-Pt(1)-N(1)	95.12(20)	C(9)-C(8)-C(13)	118.2(9)
Cl(2)-Pt(1)-N(12)	175.50(21)	C(8)-C(9)-C(10)	120.1(10)
Cl(2)-Pt(1)-C(13)	149.83(22)	C(9)-C(10)-C(11)	120.1(10)
Cl(2)-Pt(1)-C(14)	120.37(25)	C(10)-C(11)-N(12)	120.3(9)
N(1)-Pt(1)-N(12)	81.3(3)	Pt(1)-N(12)-C(11)	126.9(6)
N(1)-Pt(1)-C(13)	55.1(3)	Pt(1)-N(12)-C(13)	113.6(6)
N(1)-Pt(1)-C(14)	25.4(3)	C(11)-N(12)-C(13)	119.1(8)
N(12)-Pt(1)-C(13)	26.3(3)	Pt(1)-C(13)-C(8)	162.2(7)
N(12)-Pt(1)-C(14)	55.9(3)	Pt(1)-C(13)-N(12)	40.2(4)
C(13)-Pt(1)-C(14)	29.7(3)	Pt(1)-C(13)-C(14)	76.2(6)
Pt(1)-N(1)-C(2)	125.3(7)	C(8)-C(13)-N(12)	122.1(9)
Pt(1)-N(1)-C(14)	114.2(7)	C(8)-C(13)-C(14)	121.6(9)
C(2)-N(1)-C(14)	120.5(10)	N(12)-C(13)-C(14)	116.2(8)
N(1)-C(2)-C(3)	119.1(11)	Pt(1)-C(14)-N(1)	40.4(5)
C(2)-C(3)-C(4)	119.9(10)	Pt(1)-C(14)-C(5)	161.4(9)
C(3)-C(4)-C(5)	118.9(10)	Pt(1)-C(14)-C(13)	74.1(5)
C(4)-C(5)-C(6)	121.3(9)	N(1)-C(14)-C(5)	121.0(11)
C(4)-C(5)-C(14)	120.6(11)	N(1)-C(14)-C(13)	114.5(9)
C(6)-C(5)-C(14)	118.1(10)	C(5)-C(14)-C(13)	124.5(11)
C(5)-C(6)-C(7)	119.2(8)	O(17)-S(1)-C(18)	105.4(5)
C(5)-C(6)-O(15)	121.9(10)	O(17)-S(1)-C(19)	103.5(6)
C(7)-C(6)-O(15)	118.8(10)	C(18)-S(1)-C(19)	99.2(7)

Torsion angles

Cl1	Pt1	N1	C2	-148.4(12)	Cl1	Pt1	N1	C14	31.7(8)
Cl2	Pt1	N1	C2	6.2(9)	Cl2	Pt1	N1	C14	-173.7(11)
N12	Pt1	N1	C2	-176.5(13)	N12	Pt1	N1	C14	3.6(8)
Cl1	Pt1	N12	C11	5.8(7)	Cl1	Pt1	N12	C13	177.9(10)
Cl2	Pt1	N12	C11	-140.2(10)	Cl2	Pt1	N12	C13	31.8(7)
N1	Pt1	N12	C11	-176.8(11)	N1	Pt1	N12	C13	-4.8(7)
Pt1	N1	C2	C3	-179.5(17)	C14	N1	C2	C3	0.4(10)
Pt1	N1	C14	C5	179.5(17)	Pt1	N1	C14	C13	-1.8(6)
C2	N1	C14	C5	-0.4(11)	C2	N1	C14	C13	178.3(21)
N1	C2	C3	C4	0.6(10)	C2	C3	C4	C5	-1.6(10)
C3	C4	C5	C6	-179.4(22)	C3	C4	C5	C14	1.6(10)
C4	C5	C6	C7	-177.5(21)	C4	C5	C6	O15	-1.3(10)
C14	C5	C6	C7	1.5(10)	C14	C5	C6	O15	177.7(23)
C4	C5	C14	N1	-0.6(9)	C4	C5	C14	C13	-179.2(21)
C6	C5	C14	N1	-179.6(21)	C6	C5	C14	C13	1.8(8)
C5	C6	C7	C8	-5.4(8)	C5	C6	C7	O16	175.6(21)
O15	C6	C7	C8	178.2(21)	O15	C6	C7	O16	-0.8(9)
C6	C7	C8	C9	-176.1(20)	C6	C7	C8	C13	6.4(9)
O16	C7	C8	C9	2.9(10)	O16	C7	C8	C13	-174.6(22)
C7	C8	C9	C10	-175.8(21)	C13	C8	C9	C10	1.7(10)
C7	C8	C13	N12	179.5(18)	C7	C8	C13	C14	-3.5(9)
C9	C8	C13	N12	1.9(9)	C9	C8	C13	C14	178.9(20)
C8	C9	C10	C11	-2.3(9)	C9	C10	C11	N12	-0.7(9)
C10	C11	N12	Pt1	175.8(15)	C10	C11	N12	C13	4.2(9)
Pt1	N12	C13	C8	-177.6(14)	Pt1	N12	C13	C14	5.3(7)
C11	N12	C13	C8	-4.9(9)	C11	N12	C13	C14	178.0(18)
C8	C13	C14	N1	-179.5(21)	C8	C13	C14	C5	-0.8(9)
N12	C13	C14	N1	-2.3(7)	N12	C13	C14	C5	176.3(21)

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Columns are 10Fo 10Fc 10Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
-12, 0, 1				0	235	186	17	3	603	611	13	1	1330	1332	8	-2	926	875	17
3	760	760	10																
4	821	810	17	-10, -4, 1				4	895	913	12	2	143	82	25	-1	1061	1061	9
4	905	888	9																
-12, 2, 1				-1	539	573	20	5	434	422	15	3	1256	1246	8	0	926	924	8
5	869	856	11																
3	478	505	10	0	833	836	9	-10, 14, 1				4	339	337	14	-8, -2, 1			
6	527	517	14																
4	633	672	17	-10, -2, 1				2	1038	1074	16	5	1293	1310	9	-3	366	345	19
7	892	899	17																
-11, -5, 1				-1	488	453	14	3	165	183	38*	6	100	53	49*	-2	1265	1249	12
-8, 12, 1																			
0	541	529	17	0	1097	1145	8	4	909	937	18	7	917	898	16	-1	836	840	9
1	912	900	14																
-11, -3, 1				-10, 0, 1				-9, -9, 1				-9, 9, 1				0	1441	1421	10
2	976	968	15																
0	721	688	17	0	978	992	11	0	645	617	12	1	991	978	10	-8, 0, 1			
3	609	582	10																
-11, -1, 1				2	791	825	13	-9, -7, 1				2	538	549	11	-2	1114	1096	17
4	1179	1191	9																
0	726	713	12	4	1124	1134	11	-2	93	123	78*	3	930	902	12	0	537	537	13
5	466	441	12																
-11, 1, 1				6	1124	1158	11	-1	1159	1120	17	4	724	697	10	2	1160	1148	9
6	1070	1090	12																
1	248	227	12	-10, 2, 1				0	498	489	13	5	770	747	9	4	1428	1452	12
7	419	419	20																
2	913	910	8	1	768	766	8	-9, -5, 1				6	581	569	11	6	1274	1277	16
-8, 14, 1																			
3	453	433	9	2	1037	1006	9	-2	743	701	20	7	721	722	15	-8, 2, 1			
1	213	206	27																
4	851	844	9	3	267	265	13	-1	1174	1134	17	-9, 11, 1				1	498	487	9
2	1357	1314	15																
5	242	218	15	4	835	839	8	0	664	661	9	1	393	369	16	2	1346	1372	7
3	15	132	473*																
6	784	838	11	5	351	337	13	-9, -3, 1				2	886	876	14	3	676	679	8
4	1143	1107	13																
-11, 3, 1				6	819	846	8	-2	739	713	14	3	865	884	11	4	1404	1445	8
5	202	118	21																
1	651	670	11	7	385	386	16	-1	946	951	9	4	897	871	10	5	699	670	12
6	939	943	19																
2	1054	1048	9	-10, 4, 1				0	1095	1093	9	5	642	642	10	6	786	774	17
-8, 16, 1																			
3	688	693	8	1	981	985	8	-9, -1, 1				6	822	829	13	7	346	312	30
1	638	665	14																
4	976	1014	8	2	915	911	8	-2	817	786	12	7	698	704	17	-8, 4, 1			
2	1008	1028	17																
5	395	390	14	3	943	935	8	-1	206	172	14	-9, 13, 1				1	866	856	8
3	585	601	19																
6	970	1008	16	4	938	932	8	0	1273	1273	9	1	422	407	19	2	1084	1086	7
4	895	905	12																
-11, 5, 1				5	997	993	9	-9, 1, 1				2	1164	1156	14	3	1161	1167	7
5	580	595	12																
1	1010	986	11	6	671	674	9	1	343	333	12	3	497	497	17	4	932	946	8
6	866	874	30																
2	316	322	13	7	795	795	14	2	1230	1187	8	4	1005	1003	13	5	1039	1063	11
-8, 18, 1																			
3	1120	1128	11	-10, 6, 1				3	180	146	17	5	316	300	15	6	760	723	16
1	1102	1141	18																
4	354	346	12	1	1280	1293	10	4	1315	1326	7	6	819	891	16	7	851	840	15
2	459	483	17																
5	840	829	17	2	175	138	17	5	498	493	11	-9, 15, 1				8	555	540	22
3	778	795	17																
6	330	319	21	3	1122	1103	8	6	1003	986	9	1	382	381	18	-8, 6, 1			
4	623	642	16																
-11, 7, 1				4	314	307	13	7	264	228	31	2	1210	1191	13	1	1741	1735	9
5	693	736	21																

```
    1  964  999   13    5  981  982    9    8  976 1063   28    3  209  199   26    2  280  275   13
-8, 20, 1
    2  210  181   18    6  180  119   32      -9,  3, 1         4 1003  987   17    3 1486 1515    7
2  232  230   29
    3 1144 1155   11    7  742  776   14    1 1071 1049    8    5  460  471   24    4  152  150   30
3  742  755   20
    4  109  114   44*    -10,  8, 1         2 1107 1103    8      -9, 17, 1         5 1134 1136   12
4   95   43   65*
    5  977  979   13    1 1048 1015   11    3  624  620    8    2  890  943   20    6  289  248   26
-7,-11, 1
     -11,  9, 1         2  540  541    9    4 1276 1293    8    3  784  846   18    7  743  719   15
0  916  924   10
    2  508  546   18    3 1209 1197   10    5  668  651   10    4  569  594   20    8  207  184   42*
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Columns are 10Fo 10Fc 10Sig, * for Insignificant

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   -2 1192 1189   31      -2,-24, 1        -1  897  898   16      -4,-16, 1           -5,-21, 1        -
2  238  205   28
   -3 1828 1844   15   -1  699  711   16   -3 1012 1023   15    0 1100 1137   14    0  114   79   65*
-8, -8, 1
   -4  684  628   12   -2  798  808   16   -4  866  859   20   -2 1192 1185   15   -1 1043 1059   13   -
2  361  360   22
   -5 1351 1368   13   -3  747  751   16   -5  875  861   23   -3  870  847   16   -2  134  173   46*
-8,-10, 1
   -6  383  372   19      -2,-26, 1           -3,-19, 1        -4 1122 1096   19      -5,-23, 1        -
1  710  670   18
   -7  821  854   23   -1  372  369   33    0  622  621   18      -4,-18, 1         0  562  579   19   -
2  779  731   17
     -2,-10, 1           -3, -1, 1        -1 1256 1290   16    0  884  874   16   -1 1032 1047   24
-8,-12, 1
```

```
 Friedel                                                    28-Mar-2003   Page10
     Columns are  10Fo   10Fc    10Sig, * for Insignificant
    l  kFo   Fc  Sig    l  kFo   Fc  Sig    l  kFo   Fc  Sig    l  kFo   Fc  Sig    l  kFo   Fc  Sig
l  kFo   Fc  Sig
     -8,-12, l         -1  458  402   22     0 1363 1361   19   -1 1038 1041   15    0  824  811   13
-10, -8, l
    0  933  944   11       -8,-14, l            -9, -9, l            -9,-11, l         -1  474  426   25
0  296  278   20
```

$\{[Pd(dpk)_2][PF_6]_2\}_n$ (polymer)

```
    Space Group and Cell Dimensions    Monoclinic,   C 2/c
 a  12.5072(16)   b  11.3498(15)   c   9.9777(14)
 beta  95.641(3)
        Volume  1409.5(3)A**3

 Empirical formula : C11 H8 F6 N2 O P Pd

 Cell dimensions were obtained from  939 reflections with 2Theta angle
 in the range   5.00 -  60.00 degrees.

 Crystal dimensions :  0.20  X  0.15  X  0.15  mm

 FW =    435.56     Z =    4     F(000) =     841.11

 Dcalc  2.053Mg.m-3, mu   1.50mm-1, lambda 0.71073A, 2Theta(max)  60.0

 The intensity data were collected on a Bruker SMART 1K diffractometer,
 using the omega scan mode.
 The h,k,l ranges used during structure solution and refinement are :--
 Hmin,max  -17  17;  Kmin,max    0  15;  Lmin,max   0  14
 No. of reflections measured                        8671
 No. of unique reflections                          2051
 No. of reflections with Inet > 2.5sigma(Inet)      1678
 Merging R-value on intensities  0.031
 Correction was made for absorption using SADABS


        Details of the last least squares cycle
   17 atoms,  121 parameters  Full-matrix    on Fo     Counter wts (k 0.000100)
 The residuals are as follows :--
 Significant reflections:  1678  Rf 0.026, Rw 0.030
 All reflections:          2051  Rf 0.035, Rw 0.032
 Included reflections:     1678  Rf 0.026, Rw 0.030  GoF  1.5053
   where Rf = Sum(Fo-Fc)/Sum(Fo),
         Rw = Sqrt[Sum(w(Fo-Fc)**2)/Sum(wFo**2)] and
        GoF = Sqrt[Sum(w(Fo-Fc)**2)/(No. of reflns - No. of params.)]
 The maximum shift/sigma ratio was  0.000.

 Last D-map:  Minimum density -0.410e/A**3,  Maximum density   0.440e/A**3.

 Secondary ext. coeff.    0.1588microns     sigma    0.0305
```

The following references are relevant to the NRCVAX System.

1. Full System Reference :
Gabe, E.J., Le Page, Y., Charland,.J.-P., Lee, F.L. and White, P.S. (1989) J. Appl. Cryst., 22, 384-387.

2. Scattering Factors from Int. Tab. Vol. 4 :
International Tables for X-ray Crystallography, Vol. IV, (1974) Kynoch Press, Birmingham, England.

The following references may also be relevant.

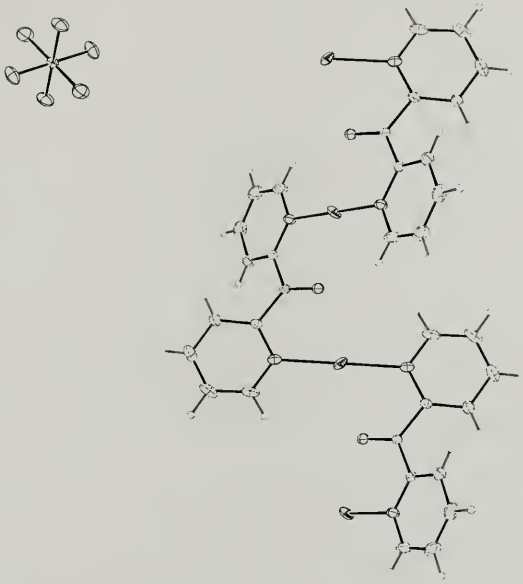
3. ORTEP Plotting :
Johnson, C.K., (1976) ORTEP - A Fortran Thermal Ellipsoid Plot Program, Technical Report ORNL-5138, Oak Ridge

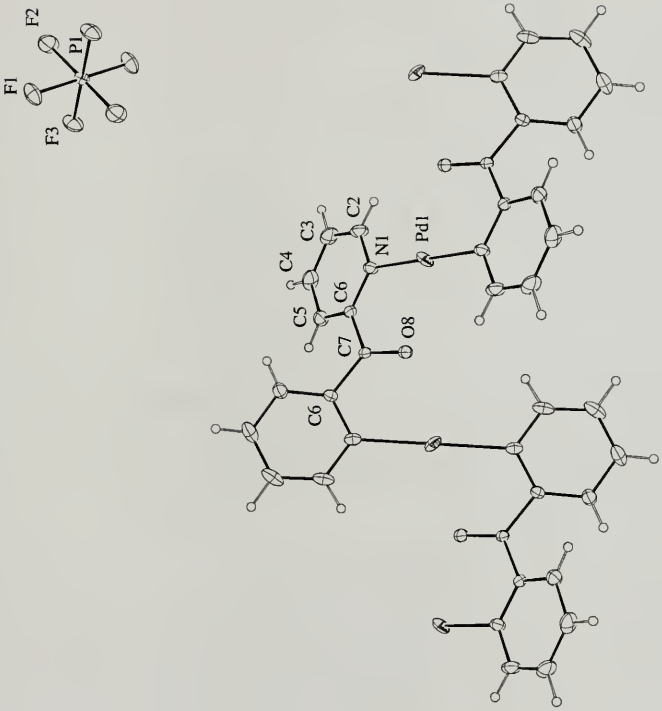
4. Pluto Plotting :
S. Motherwell, University Chemical Laboratory, Cambridge, 1978

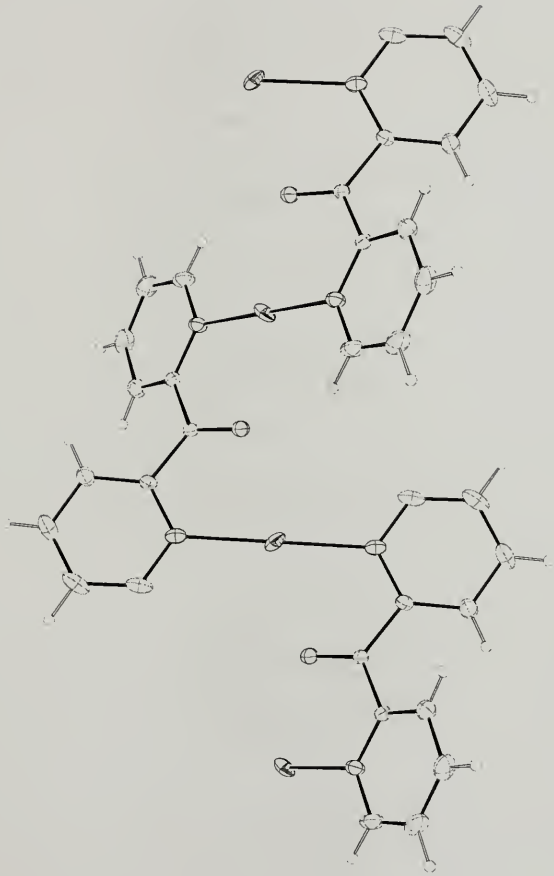
5. Missing Symmetry Treatment by MISSYM :
Le Page, Y., (1988) J. Appl. Cryst., 21, 983-984.

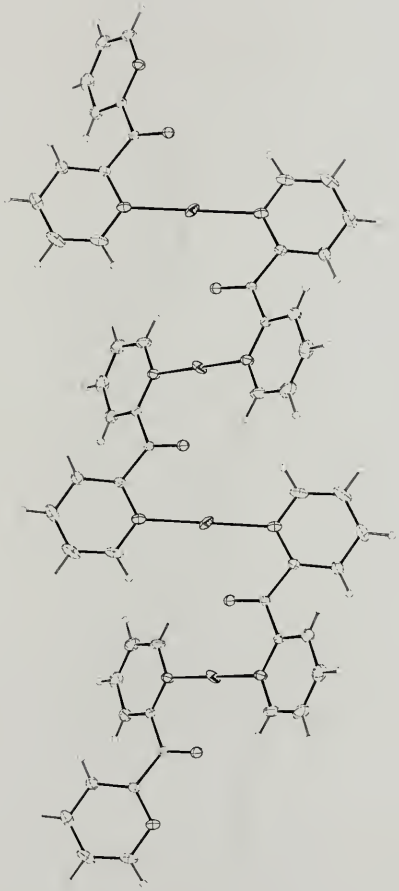
6. Grouping of Equivalent Reflections in DATRD2 :
Le Page, Y. and Gabe, E.J., (1979) J. Appl. Cryst., 12, 464-466.

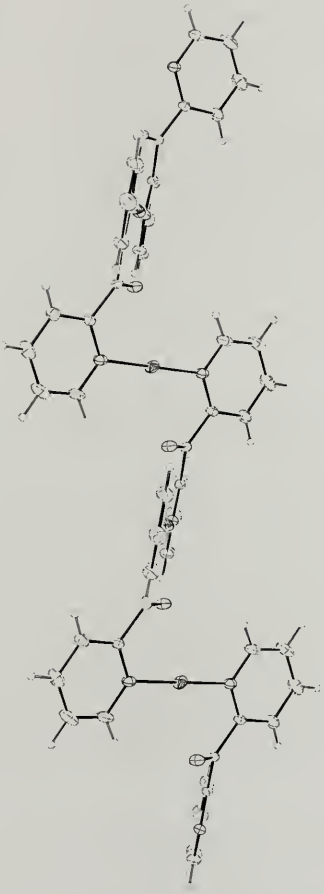
7. Extinction Treatment :
Larson, A.C., (1970) p.293, Crystallographic Computing, Munksgaard, Copenhagen.




F2
P1
F1
F3
C2
C3
N1
Pd1
C4
C6
C5
C7
O8
C6







18-Nov-2002

Table . Atomic Parameters x,y,z and Biso.
E.S.Ds. refer to the last digit printed.

	x	y	z	Biso
Pd1	1/2	0	0	2.656(11)
N1	0.43914(14)	0.17902(16)	0.01282(15)	2.14 (6)
C2	0.39012(19)	0.23377(25)	-0.09553(20)	3.04 (10)
C3	0.34436(22)	0.3438 (3)	-0.0903 (3)	3.76 (10)
C4	0.34705(22)	0.40112(25)	0.0325 (3)	3.52 (10)
C5	0.39914(19)	0.34598(21)	0.14593(23)	2.54 (8)
C6	0.44512(15)	0.23705(18)	0.13232(17)	1.77 (6)
C7	1/2	0.17031(24)	1/4	1.64 (10)
O8	1/2	0.06267(18)	1/4	2.35 (9)
P1	1/4	3/4	1	1.95 (3)
F1	0.36157(11)	0.69188(13)	1.05526(15)	3.64 (6)
F2	0.22778(14)	0.64453(13)	0.89532(14)	4.18 (7)
F3	0.30801(12)	0.82391(13)	0.89077(14)	3.51 (6)
H2	0.3899 (20)	0.1902 (22)	-0.176 (3)	3.0 (5)
H3	0.3082 (25)	0.383 (3)	-0.171 (3)	5.1 (7)
H4	0.316 (3)	0.476 (3)	0.042 (3)	4.0 (7)
H5	0.4034 (21)	0.3808 (23)	0.228 (3)	3.2 (6)

Biso is the Mean of the Principal Axes of the Thermal Ellipsoid

Table of u(i,j) or U values *100.
E.S.Ds. refer to the last digit printed

	u11(U)	u22	u33	u12	u13	u23
Pd1	3.607(14)	3.633(16)	2.842(13)	-0.048(11)	0.264(9)	-1.734(10)
N1	2.71 (8)	3.49 (10)	1.89 (7)	-0.47 (7)	-0.05 (6)	-0.21 (7)
C2	3.84 (12)	5.62 (16)	1.94 (9)	-0.87 (12)	-0.49 (8)	0.54 (10)
C3	4.73 (14)	5.29 (17)	3.88 (13)	-0.72 (12)	-1.49 (11)	2.14 (12)
C4	4.55 (14)	2.99 (14)	5.55 (15)	0.32 (11)	-0.90 (11)	1.31 (11)
C5	3.65 (11)	2.62 (11)	3.25 (11)	0.12 (9)	-0.25 (9)	0.17 (9)
C6	2.45 (9)	2.31 (10)	1.94 (8)	-0.26 (8)	0.06 (6)	0.33 (7)
C7	2.67 (13)	2.02 (13)	1.59 (11)	0.0	0.45 (9)	0.0
O8	4.81 (13)	2.04 (11)	2.07 (9)	0.0	0.40 (8)	0.0
P1	2.47 (3)	2.71 (4)	2.20 (3)	-0.15 (3)	0.111(25)	0.33 (3)
F1	2.80 (7)	4.80 (9)	6.08 (9)	0.46 (6)	-0.27 (6)	1.95 (7)
F2	8.24 (12)	3.70 (8)	3.69 (7)	-0.36 (8)	-0.74 (7)	-0.74 (6)
F3	4.10 (8)	5.35 (9)	4.02 (7)	-0.41 (7)	1.06 (6)	2.06 (7)
H2	3.8(7)					
H3	6.4(9)					
H4	5.1(9)					
H5	4.1(7)					

Anisotropic Temperature Factors are of the form
Temp=-2*Pi*Pi*(h*h*u11*astar*astar+---+2*h*k*u12*astar*bstar+---)

DISANG -- The NRCVAX Distance and Angle Program

The Space Group is C 2/C Centrosymmetric
The Equivalent Positions are:
1) x y z 2) -x y 1/2-z

The Lattice is C-centred. The Centering Vectors are:
1) 0, 0, 0 2) 1/2, 1/2, 0

There are Symmetry Equivalent atoms.
The Bond and Angle Tables may need editting.

The following Atoms are the Symmetry Equivalents

Name	x	y	z			
N(1)a	0.56086	-0.17902	-0.01282	1.000-x	-y	-z
C(6)b	0.55488	0.23705	0.36768	1.000-x	y	0.500-z
F(1)c	0.13843	0.80812	0.94474	0.500-x	1.500-y	2.000-z
F(2)c	0.27222	0.85547	1.10468	0.500-x	1.500-y	2.000-z
F(3)c	0.19199	0.67609	1.10923	0.500-x	1.500-y	2.000-z

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Pd(1)-N(1)	2.1779(19)	C(5)-H(5)	0.91(3)
Pd(1)-N(1)a	2.1779(19)	C(6)-C(7)	1.5051(22)
N(1)-C(2)	1.342(3)	C(7)-C(6)b	1.5051(22)
N(1)-C(6)	1.3577(24)	C(7)-O(8)	1.222(3)
C(2)-C(3)	1.377(4)	P(1)-F(1)	1.5922(13)
C(2)-H(2)	0.94(3)	P(1)-F(1)c	1.5922(13)
C(3)-C(4)	1.384(4)	P(1)-F(2)	1.5951(14)
C(3)-H(3)	0.99(3)	P(1)-F(2)c	1.5951(14)
C(4)-C(5)	1.398(3)	P(1)-F(3)	1.6041(13)
C(4)-H(4)	0.94(3)	P(1)-F(3)c	1.6041(13)
C(5)-C(6)	1.376(3)		

N(1)-Pd(1)-N(1)a	180.0	C(6)-C(7)-C(6)b	119.56(21)
Pd(1)-N(1)-C(2)	121.29(15)	C(6)-C(7)-O(8)	120.22(12)
Pd(1)-N(1)-C(6)	120.98(13)	C(6)b-C(7)-O(8)	120.22(12)
C(2)-N(1)-C(6)	117.66(19)	F(1)-P(1)-F(1)c	180.0
N(1)-C(2)-C(3)	123.23(21)	F(1)-P(1)-F(2)	90.35(8)
N(1)-C(2)-H(2)	114.0(15)	F(1)-P(1)-F(2)c	89.65(8)
C(3)-C(2)-H(2)	122.7(15)	F(1)-P(1)-F(3)	90.71(7)
C(2)-C(3)-C(4)	119.08(21)	F(1)-P(1)-F(3)c	89.29(7)
C(2)-C(3)-H(3)	122.5(18)	F(1)c-P(1)-F(2)	89.65(8)
C(4)-C(3)-H(3)	118.4(18)	F(1)c-P(1)-F(2)c	90.35(8)
C(3)-C(4)-C(5)	118.4(3)	F(1)c-P(1)-F(3)	89.29(7)
C(3)-C(4)-H(4)	122.8(21)	F(1)c-P(1)-F(3)c	90.71(7)
C(5)-C(4)-H(4)	118.8(21)	F(2)-P(1)-F(2)c	180.0
C(4)-C(5)-C(6)	119.24(22)	F(2)-P(1)-F(3)	90.51(8)
C(4)-C(5)-H(5)	121.2(16)	F(2)-P(1)-F(3)c	89.49(8)
C(6)-C(5)-H(5)	119.6(16)	F(2)c-P(1)-F(3)	89.49(8)
N(1)-C(6)-C(5)	122.35(17)	F(2)c-P(1)-F(3)c	90.51(8)
N(1)-C(6)-C(7)	114.99(17)	F(3)-P(1)-F(3)c	180.0
C(5)-C(6)-C(7)	122.56(17)		

Torsion angles

Pd1	N1	C2	C3	175.7(4)	Pd1	N1	C2	H2	-4. (3)
C6	N1	C2	C3	-1.32(23)	C6	N1	C2	H2	179. (3)
Pd1	N1	C6	C5	-174.2(3)	Pd1	N1	C6	C7	2.37(11)
C2	N1	C6	C5	2.81(24)	C2	N1	C6	C7	179.4(4)
N1	C2	C3	C4	-0.98(23)	N1	C2	C3	H3	-180. (3)
H2	C2	C3	C4	179. (3)	H2	C2	C3	H3	0. (4)
C2	C3	C4	C5	1.81(23)	C2	C3	C4	H4	-179. (3)
H3	C3	C4	C5	-179. (3)	H3	C3	C4	H4	0. (4)
C3	C4	C5	C6	-0.40(23)	C3	C4	C5	H5	179. (3)
H4	C4	C5	C6	-180. (3)	H4	C4	C5	H5	0. (4)
C4	C5	C6	N1	-1.98(23)	C4	C5	C6	C7	-178.3(4)
H5	C5	C6	N1	178. (3)	H5	C5	C6	C7	2. (3)
N1	C6	C7	O8	-27.02(18)	C5	C6	C7	O8	149.5(4)

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
-17, 1, 1				5	110	92	146	5	99	113	99	3	103	131	85	7	26	55	374*	5	202	195	242
1	158	145	94	6	265	267	84	6	295	293	60	4	100	104	109	8	343	346	71	-10, 0, 1			
2	226	231	75	7	66	57	463*	7	210	208	66	5	28	3	373*	9	57	7	212*	2	164	164	79
3	61	30	204*	-15, 7, 1				8	345	328	64	6	268	266	69	10	282	256	102	4	120	125	95
4	243	251	72	1	62	84	220*	9	164	159	83	7	168	183	83	11	30	29	595*	6	175	180	127
-17, 3, 1				2	202	181	124	10	185	189	98	8	230	240	75	-11, 3, 1				8	434	430	133
1	64	84	191*	3	237	239	113	-13, 3, 1				9	64	50	205*	1	141	155	62	10	224	209	140
2	97	97	144	4	147	138	133	1	183	178	65	10	56	85	335*	2	239	244	65	12	230	233	158
3	37	8	338*	5	156	164	122	2	405	419	63	-12, 4, 1				3	295	316	65	-10, 2, 1			
-16, 0, 1				-14, 0, 1				3	31	18	278*	1	282	285	70	4	401	408	61	1	36	51	179*
2	354	360	94	2	272	264	85	4	314	324	71	2	640	668	92	5	235	240	60	2	952	971	123
4	281	281	93	4	397	389	90	5	121	119	101	3	87	101	130	6	632	654	78	3	150	150	72
6	181	180	114	6	182	183	100	6	311	321	72	4	525	536	71	7	163	170	75	4	909	940	102
-16, 2, 1				8	217	227	98	7	191	182	84	5	30	13	337*	8	380	397	64	5	25	15	338*
1	112	98	99	-14, 2, 1				8	213	217	83	6	414	410	66	9	79	88	187*	6	744	748	87
2	110	92	109	1	45	24	190*	9	149	149	144	7	29	39	377*	10	207	217	96	7	243	247	60
3	32	17	358*	2	367	369	56	10	212	216	122	8	385	372	82	11	184	190	112	8	536	544	80
4	204	198	73	3	69	63	142*	-13, 5, 1				9	27	7	578*	-11, 5, 1				9	60	61	241*
5	37	19	301*	4	335	349	61	1	86	99	151	10	329	345	89	1	94	91	102	10	349	341	79
6	146	156	95	5	35	9	259*	2	342	353	73	-12, 6, 1				2	624	625	78	11	42	58	411*
-16, 4, 1				6	352	346	63	3	93	99	144	1	142	154	105	3	53	28	201*	12	287	264	108
1	98	81	123	7	7	56	1476*	4	380	390	67	2	131	127	95	4	419	421	63	-10, 4, 1			
2	311	297	69	8	290	281	67	5	73	94	166*	3	175	173	79	5	124	119	91	1	24	29	329*
3	81	84	158	9	37	50	338*	6	271	272	69	4	239	225	69	6	237	234	65	2	648	667	78
4	205	205	77	-14, 4, 1				7	272	274	72	5	45	39	267*	7	74	74	146	3	123	119	83
5	37	28	321*	1	20	0	548*	8	223	222	96	6	229	233	72	8	298	298	79	4	508	513	67
-16, 6, 1				2	254	250	63	9	159	164	127	7	71	109	229*	9	61	69	263*	5	168	154	68
1	34	23	395*	3	30	59	346*	-13, 7, 1				8	150	164	124	10	331	316	86	6	169	170	69
2	139	170	106	4	144	137	104	1	122	106	157	9	58	89	290*	-11, 7, 1				7	129	129	84
3	31	41	454*	5	79	49	161*	2	314	308	70	-12, 8, 1				1	20	39	580*	8	101	89	136
-15, 1, 1				6	112	136	127	3	122	150	118	1	84	25	198*	2	370	373	64	9	38	17	363*
1	104	103	103	7	33	55	420*	4	238	232	76	2	472	478	83	3	87	101	139	10	255	267	85
2	241	248	67	8	134	143	125	5	31	7	432*	3	70	52	233*	4	384	380	65	11	36	64	469*
3	108	115	99	-14, 6, 1				6	304	299	72	4	333	319	80	5	128	136	101	-10, 6, 1			
4	284	298	64	1	32	25	368*	7	29	43	625*	5	34	49	410*	6	354	356	66	1	80	79	114
5	104	92	104	2	356	343	80	8	245	252	100	6	338	325	86	7	258	264	86	2	364	360	61
6	279	274	67	3	31	2	446*	-13, 9, 1				7	87	110	275*	8	271	260	88	3	222	212	63
7	38	58	317*	4	461	453	83	1	129	130	148	8	211	215	131	9	200	187	104	4	353	344	60
8	307	299	70	5	73	28	186*	2	281	271	121	-12, 10, 1				-11, 9, 1				5	202	202	67
-15, 3, 1				6	400	391	71	3	118	95	170	1	25	26	888*	1	112	119	155	6	608	621	76
1	58	31	173*	7	51	51	291*	4	151	149	164	2	179	189	136	2	322	337	80	7	159	171	97
2	314	316	65	-14, 8, 1				5	110	124	217	3	28	56	786*	3	105	78	162	8	572	593	90
3	140	157	84	1	27	31	730*	6	153	164	319*	4	109	131	217	4	255	254	103	9	29	59	511*
4	265	253	68	2	105	134	205	-12, 0, 1				5	19	76	2284*	5	71	36	299*	10	277	272	86
5	82	90	137	3	22	69	773*	2	779	819	105	6	172	195	264	6	357	344	161	11	92	124	220*
6	114	131	106	4	30	24	602*	4	968	979	154	-11, 1, 1				7	125	56	369*	-10, 8, 1			
7	116	86	104	5	61	80	309*	6	452	465	91	1	218	222	48	8	175	156	281	1	63	45	235*
-15, 5, 1				-13, 1, 1				8	436	434	92	2	607	632	74	-11, 11, 1				2	465	466	66
1	77	75	159*	1	170	172	56	10	389	372	93	3	246	247	47	1	121	146	201	3	72	74	167*
2	235	213	72	2	314	323	48	-12, 2, 1				4	582	597	72	2	185	184	140	4	333	334	56
3	140	148	96	3	306	316	52	1	116	118	74	5	259	261	64	3	66	97	355*	5	95	74	117
4	227	236	89	4	396	401	62	2	118	126	72	6	278	262	66	4	110	121	227*	6	249	236	71

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
-10, 8, l				7	116	126	95	5	93	90	72	8	92	92	301*	11	85	98	151	3	391	403	37
7	234	235	92	8	350	355	63	6	532	539	53	9	162	174	177	12	278	278	79	4	1179	1182	101
8	53	47	328*	9	287	292	67	7	63	68	116	-8, 12, l				-7, 7, l				5	356	349	40
9	124	148	197	10	228	232	78	8	505	511	54	1	27	25	648*	1	309	301	48	6	982	979	86
-10, 10, l				11	186	183	94	9	21	6	460*	2	314	316	83	2	741	727	68	7	241	233	43
1	105	109	168	-9, 7, l				10	255	259	62	3	82	80	216*	3	411	385	47	8	860	864	85
2	391	365	76	1	258	243	47	11	234	241	75	4	394	380	107	4	675	655	64	9	122	113	84
3	27	5	614*	2	441	425	56	12	82	129	176*	5	139	117	203	5	304	305	45	10	632	630	70
4	318	305	82	3	27	1	322*	-8, 4, l				6	302	265	123	6	544	548	62	11	149	154	89
5	62	11	416*	4	288	281	53	1	82	83	81	7	177	162	184	7	477	493	59	12	474	471	73
6	381	365	110	5	95	87	101	2	771	770	64	-8, 14, l				8	238	251	60	13	82	79	188*
7	107	70	258*	6	362	356	64	3	32	42	196*	1	80	86	289*	9	231	237	74	-6, 4, l			
8	347	300	119	7	85	87	141	4	917	901	81	2	231	198	153	10	240	237	79	1	22	13	188*
-10, 12, l				8	372	365	67	5	212	204	45	-7, 1, l				11	238	235	84	2	352	358	36
1	79	67	255*	9	156	137	113	6	834	841	75	1	112	118	44	-7, 9, l				3	594	602	51
2	89	99	229*	10	352	340	84	7	273	282	46	2	479	499	42	1	163	147	76	4	546	558	57
3	41	3	485*	11	103	47	222*	8	577	593	65	3	21	7	222*	2	562	556	68	5	374	373	43
4	151	133	200	-9, 9, l				9	55	22	189*	4	1133	1131	98	3	148	125	82	6	633	641	65
5	242	204	141	1	167	185	87	10	572	585	68	5	433	431	51	4	332	314	59	7	181	184	57
-9, 1, l				2	611	622	76	11	136	117	102	6	656	645	68	5	24	3	554*	8	312	310	52
1	404	421	49	3	110	112	141	12	434	415	74	7	139	136	68	6	525	522	70	9	27	55	339*
2	573	574	69	4	379	387	74	-8, 6, l				8	516	515	60	7	55	39	226*	10	212	199	66
3	719	728	83	5	153	154	154	1	80	67	90	9	98	77	100	8	411	394	68	11	98	108	122
4	762	752	101	6	370	367	101	2	516	498	52	10	307	299	62	9	26	19	571*	12	218	195	82
5	314	310	48	7	178	176	107	3	18	32	397*	11	31	39	386*	10	423	399	75	13	156	146	111
6	533	528	59	8	182	165	110	4	355	345	45	12	390	377	71	-7, 11, l				-6, 6, l			
7	156	157	58	9	252	235	95	5	133	114	62	13	136	123	122	1	135	145	121	1	121	116	54
8	558	550	57	-9, 11, l				6	248	244	48	-7, 3, l				2	326	314	75	2	1299	1249	111
9	62	49	143*	1	27	3	606*	7	111	124	92	1	169	153	41	3	111	101	119	3	169	163	47
10	314	307	60	2	258	241	86	8	211	208	64	2	1481	1430	117	4	222	223	88	4	776	759	70
11	265	247	74	3	72	92	250*	9	196	191	69	3	59	63	81	5	309	309	81	5	61	58	120
12	268	269	89	4	299	294	111	10	68	58	184*	4	606	593	57	6	151	143	131	6	397	398	52
-9, 3, l				5	108	11	261*	11	227	231	75	5	290	286	41	7	191	186	110	7	17	64	495*
1	558	554	68	6	348	345	114	-8, 8, l				6	645	663	60	8	253	229	99	8	545	565	63
2	966	955	86	7	56	71	523*	1	126	135	94	7	410	422	47	9	265	242	118	9	30	22	338*
3	373	385	57	-9, 13, l				2	862	847	96	8	695	717	73	-7, 13, l				10	537	533	66
4	644	651	67	1	52	63	399*	3	161	165	59	9	63	58	148*	1	12	39	1274*	11	110	107	142
5	137	130	62	2	153	164	144	4	603	595	59	10	489	507	62	2	173	172	116	12	310	310	78
6	500	493	57	3	172	162	167	5	100	93	92	11	83	81	144	3	37	25	691*	-6, 8, l			
7	72	82	114	4	208	202	165	6	646	645	78	12	206	208	86	4	374	354	96	1	124	131	83
8	370	364	62	-8, 0, l				7	28	67	431*	13	168	150	107	5	108	95	194	2	240	218	44
9	84	95	140	2	916	956	142	8	475	469	69	-7, 5, l				6	331	320	92	3	85	81	87
10	360	346	68	4	1041	1060	156	9	66	37	221*	1	224	226	41	-6, 0, l				4	329	329	49
11	28	45	601*	6	405	389	67	10	523	507	77	2	535	540	48	2	745	777	114	5	51	64	201*
12	300	263	86	8	467	458	74	-8, 10, l				3	24	8	240*	4	1110	1083	135	6	610	617	74
-9, 5, l				10	316	316	91	1	125	138	126	4	676	674	62	6	323	321	59	7	230	230	66
1	355	347	45	12	484	449	106	2	152	144	104	5	271	264	43	8	401	422	68	8	226	231	70
2	402	393	51	-8, 2, l				3	23	35	662*	6	533	528	54	10	112	124	136	9	127	141	119
3	338	335	49	1	55	52	100	4	117	113	146	7	270	261	52	12	164	175	132	10	247	250	80
4	547	553	69	2	648	619	60	5	164	161	142	8	370	378	55	-6, 2, l				11	124	132	139
5	37	18	218*	3	528	525	47	6	201	207	137	9	40	9	242*	1	407	402	37	-6, 10, l			
6	519	513	60	4	554	540	53	7	106	64	241*	10	330	325	60	2	1415	1418	112	1	133	136	106

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-6, 10, 1			13	30	34	478*	2	195	207	99	7	218	218	52	7	471	470	48	4	488	493	63
2	810	836	89		-5, 5, 1			3	119	120	140	8	419	434	55	8	687	701	79	5	288	294	58
3	85	97	140	1	45	27	105*	4	317	317	81	9	89	102	108	9	478	498	57	6	633	650	77
4	516	533	78	2	736	730	65	5	219	184	106	10	348	351	67	10	329	326	60	7	126	127	97
5	193	178	88	3	604	602	56	6	354	348	87	11	134	157	112	11	73	99	149*	8	273	280	66
6	531	544	83	4	528	518	51	7	186	188	123	12	85	109	182*	12	377	386	69	9	71	77	179*
7	56	8	293*	5	680	674	62		-5, 15, 1				-4, 8, 1			13	128	147	115	10	375	373	72
8	398	396	82	6	577	580	62	1	121	103	194	1	25	34	333*		-3, 3, 1			11	33	31	447*
9	212	203	86	7	344	348	50	2	250	236	137	2	1227	1202	106	1	518	522	52		-3, 11, 1		
10	365	336	76	8	494	508	59	3	92	15	394*	3	233	227	47	2	501	503	51	1	456	476	63
	-6, 12, 1			9	197	204	61		-4, 0, 1			4	754	753	75	3	699	721	68	2	447	455	62
1	123	111	134	10	316	316	56	2	244	266	51	5	255	265	56	4	591	581	60	3	45	62	295*
2	170	158	105	11	314	296	62	4	1796	1791	215	6	692	712	80	5	373	379	45	4	489	493	78
3	35	14	433*	12	233	247	80	6	1391	1409	168	7	184	202	72	6	860	831	84	5	208	208	90
4	195	212	98	13	175	164	125	8	1144	1176	140	8	401	402	65	7	638	640	66	6	390	401	78
5	148	123	128		-5, 7, 1			10	439	459	91	9	48	8	268*	8	776	788	78	7	232	224	89
6	77	81	243*	1	728	721	72	12	464	476	100	10	538	529	75	9	356	370	52	8	316	323	84
7	150	151	137	2	942	904	83		-4, 2, 1			11	134	117	121	10	661	672	71	9	370	345	86
8	163	147	144	3	506	495	51	1	1132	1116	90		-4, 10, 1			11	263	270	65	10	240	228	110
	-6, 14, 1			4	526	509	52	2	1613	1568	138	1	173	180	81	12	343	343	67		-3, 13, 1		
1	39	65	450*	5	327	320	48	3	615	617	55	2	353	355	57	13	108	125	133	1	120	125	142
2	275	279	121	6	617	621	66	4	749	746	66	3	44	46	250*		-3, 5, 1			2	268	274	81
3	79	70	351*	7	138	137	84	5	372	377	45	4	237	232	77	1	59	63	78	3	43	10	346*
4	293	293	90	8	529	524	70	6	177	177	51	5	211	217	86	2	1132	1124	97	4	239	232	90
5	111	108	195	9	10	34	1257*	7	22	4	324*	6	369	368	75	3	199	205	34	5	62	18	283*
	-5, 1, 1			10	419	424	68	8	430	441	53	7	117	108	140	4	1103	1097	105	6	242	228	99
1	264	248	32	11	30	12	498*	9	434	422	55	8	254	251	70	5	58	58	112	7	79	25	264*
2	666	662	59	12	226	240	93	10	476	491	68	9	292	290	73	6	822	823	81		-3, 15, 1		
3	55	51	90		-5, 9, 1			11	30	21	341*	10	211	212	89	7	133	136	65	1	111	103	190
4	683	667	67	1	635	622	84	12	302	291	68		-4, 12, 1			8	459	474	56	2	232	224	140
5	182	167	42	2	552	551	67	13	57	50	249*	1	63	66	239*	9	29	5	299*	3	165	151	126
6	508	509	50	3	447	451	60		-4, 4, 1			2	307	313	63	10	283	282	57	4	206	210	111
7	327	344	44	4	569	573	81	1	397	365	40	3	26	36	543*	11	58	52	191*		-2, 0, 1		
8	726	730	67	5	182	168	69	2	1418	1406	120	4	470	489	80	12	310	302	69	2	218	207	69
9	296	292	52	6	608	638	75	3	327	335	37	5	26	7	612*	13	31	52	544*	4	1771	1703	261
10	321	315	60	7	122	124	106	4	1486	1486	126	6	448	438	83		-3, 7, 1			6	600	576	68
11	267	263	66	8	235	246	73	5	519	520	50	7	50	48	366*	1	238	232	39	8	184	169	58
12	316	317	69	9	368	360	69	6	1364	1375	129	8	391	383	88	2	1035	1016	90	10	91	82	151
13	33	8	422*	10	325	317	74	7	206	212	53		-4, 14, 1			3	426	423	44	12	457	453	99
	-5, 3, 1			11	298	294	79	8	674	682	71	1	102	99	184	4	570	562	59	14	261	249	114
1	475	461	42		-5, 11, 1			9	407	402	55	2	231	248	132	5	99	106	78		-2, 2, 1		
2	1564	1557	123	1	149	141	101	10	360	361	56	3	73	3	243*	6	522	521	66	1	186	185	27
3	215	208	30	2	427	433	62	11	207	197	67	4	175	174	114	7	66	65	149*	2	1680	1694	175
4	1738	1753	162	3	162	163	83	12	417	407	70	5	165	144	136	8	504	503	68	3	346	343	39
5	377	386	42	4	242	239	80	13	33	48	443*	6	82	69	273*	9	133	125	94	4	1428	1422	133
6	1050	1052	91	5	191	213	96		-4, 6, 1				-3, 1, 1			10	475	484	70	5	643	621	58
7	126	117	69	6	126	105	142	1	140	130	45	1	2335	2335	219	11	239	247	78	6	1078	1115	94
8	529	547	60	7	28	40	582*	2	483	467	52	2	1971	1970	205	12	262	254	82	7	228	223	41
9	208	188	57	8	244	244	96	3	275	266	38	3	91	112	52		-3, 9, 1			8	1115	1142	107
10	587	594	67	9	32	45	621*	4	353	340	41	4	1823	1807	169	1	410	420	65	9	26	9	316*
11	86	82	133		-5, 13, 1			5	173	163	52	5	275	288	40	2	732	717	81	10	741	761	88
12	404	406	69	1	26	56	630*	6	324	327	49	6	829	822	73	3	79	71	125	11	38	47	268*

Columns are 10Fo 10Fc 100Sig, * for Insignificant

1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig
	-2, 2, 1			8	493	486	70	4	1199	1206	113	6	211	211	99	6	420	415	51		1, 1, 1		
12	357	372	67	9	154	155	100	5	793	784	88	7	216	189	109	7	252	255	47	1	1205	1237	142
13	45	59	305*	10	584	575	93	6	796	801	72	8	284	275	99	8	479	484	65	2	1151	1151	109
	-2, 4, 1				-2, 12, 1			7	477	489	55		-1, 15, 1			9	29	38	319*	3	91	87	38
1	249	239	36	1	102	112	114	8	619	651	74	1	26	58	886*	10	383	388	66	4	1494	1472	129
2	1224	1211	114	2	214	212	71	9	127	118	73	2	162	177	166	11	71	104	177*	5	430	420	40
3	701	666	68	3	66	103	211*	10	467	477	60	3	30	26	571*	12	262	262	88	6	685	664	58
4	263	250	42	4	330	338	75	11	245	232	64	4	217	224	108		0, 8, 1			7	15	26	333*
5	474	451	47	5	41	54	364*	12	310	318	83		0, 0, 1			0	735	720	112	8	736	748	63
6	434	425	45	6	180	219	108	13	396	356	87	2	3407	3387	523	1	118	108	58	9	619	626	61
7	155	171	56	7	61	39	294*		-1, 7, 1			4	963	958	119	2	928	925	88	10	473	484	53
8	560	571	62	8	134	123	147	1	98	77	37	6	675	672	88	3	132	121	57	11	125	120	80
9	40	56	216*	9	254	243	105	2	712	702	69	8	1403	1460	174	4	564	572	67	12	461	461	71
10	453	456	59		-2, 14, 1			3	22	24	261*	10	777	780	104	5	179	185	60	13	35	30	354*
11	139	134	93	1	60	77	302*	4	608	590	81	12	572	565	110	6	776	789	87		1, 3, 1		
12	225	229	75	2	287	297	81	5	324	314	53		0, 2, 1			7	142	134	77	0	1443	1447	171
13	130	113	124	3	60	59	280*	6	655	670	76	0	1011	1081	201	8	514	524	69	1	363	380	43
	-2, 6, 1			4	385	386	82	7	40	55	224*	1	222	226	40	9	208	221	71	2	1487	1497	140
1	593	569	59	5	124	116	153	8	511	518	68	2	371	358	43	10	521	524	73	3	747	740	72
2	1324	1341	125	6	395	383	88	9	27	26	379*	3	85	75	44	11	111	108	131	4	1008	1021	88
3	307	316	37		-1, 1, 1			10	432	448	69	4	1735	1692	138	12	328	312	79	5	195	208	36
4	1627	1621	152	1	215	206	27	11	32	11	386*	5	443	441	48		0, 10, 1			6	897	894	80
5	125	114	58	2	1288	1301	135	12	222	216	93	6	830	826	83	0	133	146	106	7	357	350	40
6	1076	1080	103	3	754	787	74		-1, 9, 1			7	169	167	40	1	246	236	66	8	570	565	53
7	135	139	66	4	1674	1636	144	1	171	174	74	8	282	268	39	2	532	545	65	9	206	195	45
8	527	535	61	5	128	120	38	2	656	643	74	9	23	32	278*	3	189	202	76	10	335	339	53
9	66	60	171*	6	1008	993	82	3	314	306	46	10	189	190	58	4	602	606	84	11	198	200	62
10	492	496	70	7	185	180	38	4	303	305	53	11	112	100	88	5	333	354	70	12	195	218	69
11	186	177	89	8	1064	1076	87	5	476	485	63	12	235	239	69	6	407	420	62	13	57	56	237*
12	495	472	87	9	101	102	79	6	608	608	74	13	17	39	747*	7	25	38	421*		1, 5, 1		
13	26	70	994*	10	554	565	63	7	276	268	61		0, 4, 1			8	83	108	143	0	1567	1557	143
	-2, 8, 1			11	132	138	88	8	304	304	63	0	912	947	184	9	196	187	82	1	107	117	47
1	267	238	58	12	378	391	67	9	311	306	67	1	246	247	41	10	177	184	99	2	799	785	85
2	500	491	54	13	48	60	286*	10	329	332	71	2	1428	1451	132		0, 12, 1			3	282	305	40
3	153	147	53		-1, 3, 1			11	328	321	75	3	860	875	82	0	756	784	172	4	838	809	74
4	343	336	53	1	797	834	99		-1, 11, 1			4	1420	1414	132	1	13	35	905*	5	608	616	57
5	256	250	56	2	1140	1137	140	1	53	59	196*	5	528	510	56	2	525	541	79	6	1029	1023	84
6	647	680	76	3	512	531	52	2	632	645	74	6	1199	1197	97	3	103	95	142	7	103	100	61
7	189	198	68	4	1005	998	107	3	158	155	98	7	242	248	43	4	431	442	76	8	867	902	73
8	273	278	64	5	872	853	83	4	646	655	89	8	759	791	71	5	180	170	95	9	98	98	80
9	235	230	70	6	764	773	76	5	25	29	562*	9	140	168	60	6	414	427	79	10	565	571	65
10	163	171	91	7	96	95	60	6	421	427	78	10	576	575	66	7	147	154	129	11	30	49	418*
11	218	199	88	8	330	329	49	7	40	19	399*	11	207	212	71	8	489	485	87	12	335	340	83
12	32	65	517*	9	94	86	89	8	339	333	83	12	382	382	69	9	185	163	128	13	72	7	243*
	-2, 10, 1			10	335	326	61	9	147	137	140	13	118	110	128		0, 14, 1				1, 7, 1		
1	22	14	511*	11	61	88	176*	10	332	330	96		0, 6, 1			0	80	102	271*	0	615	652	61
2	798	817	87	12	385	372	68		-1, 13, 1			0	1601	1583	191	1	76	53	262*	1	184	171	42
3	65	57	199*	13	144	136	108	1	23	26	681*	1	487	492	64	2	81	74	198*	2	1398	1410	129
4	322	329	69		-1, 5, 1			2	242	231	84	2	1086	1052	101	3	90	96	183*	3	516	520	54
5	491	503	77	1	148	140	36	3	67	90	232*	3	243	249	36	4	75	69	225*	4	1164	1150	122
6	335	328	73	2	1690	1723	177	4	216	230	92	4	387	382	58	5	139	144	148	5	480	492	61
7	189	194	77	3	609	611	61	5	201	204	98	5	10	49	579*	6	70	75	291*	6	568	578	80

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	1, 7, 1			8	1101	1159	139	4	46	60	153*	13	69	59	188*	7	346	350	61	13	38	4	314*
7	480	504	64	10	244	254	69	5	397	426	57		3, 3, 1			8	379	392	64		4, 4, 1		
8	196	187	66	12	189	172	112	6	198	207	60	0	954	986	90	9	291	294	69	0	1361	1334	108
9	260	260	65		2, 2, 1			7	262	262	60	1	465	464	43	10	363	366	70	1	638	645	57
10	365	372	66	0	2015	2011	189	8	201	215	68	2	1422	1420	132	11	146	143	112	2	1407	1388	121
11	308	307	72	1	703	722	68	9	118	107	100	3	322	303	36		3, 11, 1			3	158	151	35
12	346	313	87	2	1749	1765	164	10	286	295	69	4	691	688	68	0	526	533	97	4	1370	1328	118
	1, 9, 1			3	741	716	72	11	93	102	149	5	58	81	75	1	198	202	70	5	77	72	66
0	577	553	67	4	1455	1418	124		2, 10, 1			6	641	635	60	2	644	652	87	6	1125	1146	92
1	140	151	86	5	174	174	33	0	738	700	117	7	89	79	68	3	24	8	560*	7	27	49	210*
2	688	692	77	6	750	741	63	1	23	47	402*	8	658	665	59	4	575	578	83	8	749	775	66
3	209	209	52	7	145	151	44	2	796	817	87	9	180	163	49	5	148	160	106	9	142	147	58
4	177	173	58	8	594	583	54	3	346	342	68	10	484	506	55	6	288	304	77	10	516	513	58
5	64	56	131*	9	158	154	53	4	785	804	101	11	35	6	261*	7	100	100	173	11	28	39	443*
6	482	501	65	10	593	602	61	5	80	69	119	12	184	201	73	8	214	212	79	12	304	312	72
7	66	44	152*	11	23	27	374*	6	675	704	80	13	72	61	176*	9	105	113	134		4, 6, 1		
8	375	376	64	12	577	574	69	7	179	180	71		3, 5, 1				3, 13, 1			0	628	622	57
9	86	56	133	13	53	52	237*	8	348	355	65	0	1115	1124	95	0	314	324	76	1	82	73	64
10	343	350	70		2, 4, 1			9	263	269	71	1	169	148	34	1	225	238	102	2	844	830	74
11	43	47	356*	0	1617	1634	150	10	442	428	73	2	1265	1239	109	2	164	158	101	3	27	33	145*
	1, 11, 1			1	628	627	61		2, 12, 1			3	552	564	52	3	260	256	79	4	643	632	60
0	426	416	87	2	986	970	85	0	314	315	92	4	967	952	85	4	220	238	89	5	216	219	41
1	345	350	58	3	678	662	61	1	200	203	73	5	618	615	58	5	293	271	86	6	346	343	50
2	246	234	64	4	208	211	34	2	197	205	82	6	618	603	59	6	281	281	87	7	522	559	55
3	250	249	73	5	314	293	39	3	154	156	107	7	367	368	42	7	262	244	99	8	335	329	49
4	347	369	71	6	338	318	39	4	205	215	85	8	490	503	49		3, 15, 1			9	251	262	54
5	305	296	73	7	297	290	39	5	115	110	142	9	149	143	55	0	142	155	142	10	351	345	60
6	421	438	77	8	427	424	45	6	228	234	91	10	478	460	62	1	26	26	917*	11	43	70	286*
7	219	221	89	9	263	258	44	7	79	10	232*	11	181	182	81	2	98	128	248*	12	306	288	78
8	345	351	82	10	365	360	50	8	352	349	85	12	385	359	73	3	126	101	157		4, 8, 1		
9	425	414	70	11	168	169	71		2, 14, 1				3, 7, 1				4, 0, 1			0	968	964	117
10	258	244	89	12	109	110	110	0	308	308	71	0	643	619	63	0	1194	1226	265	1	146	142	51
	1, 13, 1			13	90	98	162	1	49	73	410*	1	217	208	40	2	1455	1486	178	2	1015	1031	96
0	361	382	93		2, 6, 1			2	337	345	78	2	556	542	57	4	1373	1369	145	3	357	359	53
1	87	50	150	0	858	877	81	3	28	12	589*	3	45	33	131*	6	664	649	75	4	563	568	68
2	384	392	74	1	642	651	70	4	285	304	87	4	752	757	75	8	1138	1160	144	5	94	74	89
3	80	84	190*	2	1277	1267	132	5	126	116	156	5	332	331	49	10	705	726	98	6	681	717	72
4	365	365	77	3	512	516	53	6	224	222	104	6	861	894	86	12	446	437	82	7	42	27	202*
5	28	6	571*	4	1563	1590	134		3, 1, 1			7	56	52	143*		4, 2, 1			8	477	479	56
6	176	194	117	5	57	11	93	0	2383	2392	290	8	420	410	52	0	1564	1566	133	9	137	136	91
7	45	32	437*	6	1253	1264	109	1	1205	1231	114	9	55	11	171*	1	786	788	69	10	397	388	69
	1, 15, 1			7	15	23	465*	2	1134	1145	108	10	330	319	67	2	593	599	58	11	366	344	74
0	149	174	118	8	691	713	67	3	372	353	38	11	111	116	126	3	792	775	84		4, 10, 1		
1	110	133	212	9	16	26	531*	4	1673	1624	133	12	343	317	87	4	686	676	58	0	141	125	93
2	219	226	127	10	430	437	67	5	458	448	46		3, 9, 1			5	135	141	40	1	39	48	259*
3	102	108	185	11	228	216	77	6	924	905	76	0	561	573	77	6	530	525	49	2	144	136	83
4	279	276	92	12	431	435	86	7	624	650	59	1	390	391	57	7	10	36	533*	3	102	105	124
	2, 0, 1				2, 8, 1			8	667	683	65	2	761	766	75	8	234	225	42	4	135	149	72
0	947	948	210	0	388	375	45	9	544	541	57	3	55	33	129*	9	66	62	106	5	134	137	78
2	638	625	97	1	231	227	46	10	328	326	49	4	244	246	53	10	125	137	71	6	313	320	61
4	1958	1939	238	2	575	560	59	11	305	298	51	5	183	188	61	11	244	260	55	7	59	76	185*
6	1360	1371	168	3	434	456	56	12	401	398	61	6	416	435	61	12	248	247	63	8	112	133	114

Columns are 10Fo 10Fc 100Sig, * for Insignificant

1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig
	4, 10, 1			3	622	620	62	6	172	174	121	10	471	457	59	11	127	139	88	0	250	244	82
9	137	141	100	4	772	771	64		5, 15, 1			11	108	123	137	12	231	238	67	1	32	37	377*
10	200	198	91	5	400	387	46	0	206	207	114		6, 8, 1				7, 3, 1			2	104	93	131
	4, 12, 1			6	634	619	57	1	90	73	284*	0	121	108	74	0	1795	1771	141	3	151	146	110
0	450	474	75	7	26	6	236*	2	144	168	188	1	222	213	58	1	437	438	44	4	195	180	94
1	107	100	117	8	501	517	51		6, 0, 1			2	782	772	77	2	1378	1374	109	5	108	77	158
2	522	539	79	9	33	31	257*	0	1100	1072	167	3	38	49	176*	3	390	384	40	6	250	263	70
3	106	112	142	10	313	321	56	2	759	735	83	4	585	589	64	4	681	672	62	7	59	16	244*
4	511	518	81	11	34	11	366*	4	862	842	106	5	163	171	62	5	392	388	39		7, 13, 1		
5	248	228	86	12	193	202	93	6	48	78	142*	6	371	381	55	6	389	400	43	0	272	271	79
6	285	292	87		5, 7, 1			8	110	92	99	7	189	183	63	7	179	188	48	1	177	158	136
7	210	189	101	0	966	946	93	10	184	180	82	8	100	94	99	8	366	382	46	2	360	358	93
8	334	338	89	1	432	436	46	12	336	319	96	9	37	34	267*	9	135	146	70	3	227	213	109
	4, 14, 1			2	676	658	68		6, 2, 1			10	223	233	75	10	487	476	58	4	298	303	101
0	183	200	96	3	675	687	62	0	1616	1625	139		6, 10, 1			11	32	23	325*	5	181	181	133
1	56	48	386*	4	285	266	47	1	856	855	83	0	730	744	95		7, 5, 1				8, 0, 1		
2	135	139	131	5	401	407	52	2	1224	1241	98	1	152	151	81	0	437	417	42	0	1213	1214	151
3	30	21	543*	6	437	450	56	3	83	90	60	2	492	493	74	1	237	228	37	2	869	884	95
4	141	153	131	7	368	354	49	4	1213	1235	103	3	27	39	313*	2	617	612	54	4	1233	1228	131
5	31	21	558*	8	418	427	53	5	391	390	38	4	260	262	59	3	122	111	69	6	666	667	77
	5, 1, 1			9	197	189	62	6	1111	1123	91	5	71	73	135	4	740	744	67	8	509	539	80
0	1952	1911	184	10	401	391	62	7	553	566	52	6	517	533	70	5	167	162	47	10	368	371	78
1	263	282	29	11	305	283	68	8	812	837	76	7	40	50	284*	6	566	574	53		8, 2, 1		
2	1257	1262	100		5, 9, 1			9	61	62	118	8	428	424	63	7	302	310	44	0	701	690	70
3	229	231	30	0	210	197	71	10	423	443	54	9	174	168	92	8	396	389	52	1	240	230	36
4	1081	1087	81	1	182	174	51	11	117	102	88		6, 12, 1			9	162	159	70	2	375	373	42
5	260	268	32	2	699	701	71	12	295	300	60	0	230	219	86	10	298	287	66	3	135	134	46
6	644	649	52	3	94	78	92		6, 4, 1			1	52	84	368*	11	80	53	164*	4	352	339	40
7	176	172	44	4	578	590	71	0	534	533	46	2	171	188	94		7, 7, 1			5	243	247	40
8	757	793	72	5	51	5	175*	1	623	626	53	3	206	181	89	0	585	585	52	6	482	484	48
9	117	116	67	6	453	482	64	2	700	683	59	4	192	220	99	1	234	232	46	7	80	90	85
10	442	441	54	7	46	36	226*	3	492	486	48	5	162	175	114	2	584	579	57	8	481	478	51
11	223	213	57	8	165	180	77	4	401	397	40	6	47	68	357*	3	303	295	50	9	33	40	248*
12	372	360	57	9	50	65	245*	5	170	166	44	7	87	81	220*	4	462	456	55	10	195	195	62
	5, 3, 1			10	326	302	88	6	409	404	44		6, 14, 1			5	129	129	70	11	132	110	94
0	376	386	38		5, 11, 1			7	170	179	47	0	238	252	97	6	570	584	64		8, 4, 1		
1	142	125	36	0	448	444	73	8	370	376	45	1	99	84	233*	7	63	51	138*	0	923	934	92
2	608	597	56	1	211	207	70	9	13	15	592*	2	306	296	101	8	411	410	54	1	403	412	49
3	687	681	61	2	348	351	70	10	261	261	55	3	36	25	506*	9	36	13	278*	2	1363	1337	119
4	1019	1007	82	3	50	72	274*	11	61	70	160*	4	354	343	86	10	166	178	79	3	73	58	95
5	299	308	40	4	403	409	74	12	105	112	154		7, 1, 1				7, 9, 1			4	925	919	88
6	772	771	66	5	246	256	83		6, 6, 1			0	570	583	53	0	455	465	62	5	185	196	44
7	159	156	48	6	437	425	78	0	1077	1043	87	1	495	501	51	1	207	210	64	6	409	406	45
8	321	310	43	7	61	62	196*	1	121	115	56	2	400	398	36	2	660	668	69	7	129	138	61
9	102	108	73	8	371	354	70	2	701	687	60	3	1004	1005	76	3	69	63	119	8	299	303	47
10	311	302	51		5, 13, 1			3	96	105	88	4	824	823	73	4	360	362	53	9	62	60	141*
11	313	303	55	0	317	336	78	4	682	673	64	5	407	410	39	5	123	121	79	10	459	447	64
12	239	240	68	1	23	69	777*	5	35	5	207*	6	630	627	52	6	312	300	57	11	70	53	205*
	5, 5, 1			2	258	266	78	6	648	634	69	7	296	318	41	7	228	218	64		8, 6, 1		
0	1112	1106	97	3	110	98	143	7	184	185	55	8	553	555	58	8	151	149	78	0	340	330	50
1	396	388	39	4	201	201	98	8	537	529	58	9	152	170	60	9	315	282	60	1	25	19	285*
2	1125	1124	90	5	29	4	604*	9	153	151	74	10	215	217	58		7, 11, 1			2	25	28	302*

Columns are 10Fo 10Fc 100Sig, * for Insignificant

1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig	1	kFo	Fc	Sig
	8,	6, 1		10	259	264	69	4	158	164	135	1	79	61	158	8	159	172	92	8	322	323	73
3	213	196	60	11	136	115	104	5	291	273	106	2	310	302	75	9	259	252	80		12,	6, 1	
4	212	211	57		9,	3, 1		6	177	171	96	3	103	73	159		11,	7, 1		0	240	240	78
5	52	13	182*	0	691	709	81		9,	13, 1		4	228	223	73	0	234	220	83	1	129	124	84
6	395	409	56	1	175	165	51	0	185	202	141	5	103	105	122	1	334	342	73	2	216	214	62
7	54	54	174*	2	517	532	59	1	25	1	1065*	6	220	224	81	2	298	290	75	3	69	47	170*
8	229	234	63	3	334	327	49	2	289	272	149	7	212	206	79	3	214	220	105	4	54	70	339*
9	75	66	159*	4	726	751	75	3	85	17	249*	8	53	64	253*	4	318	318	93	5	54	54	202*
10	31	14	394*	5	332	321	50		10,	0, 1			10,	10, 1		5	72	41	161*	6	56	41	212*
	8,	8, 1		6	923	952	85	0	351	354	64	0	309	302	80	6	286	292	68	7	62	64	204*
0	652	634	78	7	279	282	52	2	173	169	70	1	131	121	164	7	58	52	215*		12,	8, 1	
1	165	169	66	8	518	527	64	4	331	338	68	2	344	368	130	8	235	218	81	0	391	389	80
2	682	696	79	9	112	100	98	6	126	130	86	3	74	78	163*		11,	9, 1		1	78	84	257*
3	143	134	69	10	201	205	76	8	171	204	104	4	295	287	75	0	220	245	93	2	475	474	70
4	432	448	62		9,	5, 1		10	51	78	303*	5	126	106	112	1	233	226	93	3	26	14	688*
5	107	101	93	0	433	420	54		10,	2, 1		6	312	313	79	2	391	392	94	4	398	401	78
6	508	503	70	1	26	55	300*	0	945	950	94		10,	12, 1		3	222	212	108	5	50	38	291*
7	210	202	68	2	461	454	55	1	44	36	157*	0	128	132	175	4	273	265	77	6	419	416	73
8	427	414	62	3	31	6	226*	2	807	816	76	1	40	14	589*	5	230	228	83		12,	10, 1	
9	71	75	181*	4	377	352	56	3	181	179	52	2	24	47	1127*	6	336	317	82	0	87	117	248*
	8,	10, 1		5	113	112	67	4	699	705	68	3	24	57	1165*		11,	11, 1		1	188	150	182
0	224	216	104	6	207	197	50	5	77	68	129		11,	1, 1		0	358	344	103	2	123	123	269*
1	51	67	275*	7	67	57	141*	6	581	587	67	0	633	646	63	1	22	18	1314*	3	75	56	199*
2	424	438	70	8	247	252	63	7	58	27	135*	1	139	141	58	2	269	272	146	4	89	72	180*
3	32	17	313*	9	81	70	156	8	477	482	71	2	417	420	50	3	91	94	361*		13,	1, 1	
4	248	255	70	10	343	301	84	9	63	64	174*	3	28	14	282*	4	144	166	225	0	360	366	50
5	66	103	150*		9,	7, 1		10	345	319	70	4	529	537	58		12,	0, 1		1	36	73	219*
6	203	196	73	0	543	530	63		10,	4, 1		5	39	23	267*	0	610	616	87	2	255	252	51
7	36	34	338*	1	46	52	195*	0	337	337	56	6	348	351	49	2	219	227	70	3	31	16	283*
8	105	111	135	2	660	667	70	1	154	154	60	7	132	129	76	4	437	437	77	4	403	402	55
	8,	12, 1		3	25	15	464*	2	340	349	51	8	319	318	65	6	388	383	73	5	268	261	68
0	328	320	81	4	423	431	62	3	97	92	88	9	85	71	132	8	402	374	98	6	318	310	58
1	82	49	348*	5	121	118	90	4	348	356	52		11,	3, 1			12,	2, 1		7	248	234	70
2	265	272	96	6	313	320	62	5	25	38	475*	0	409	416	53	0	431	446	56	8	239	238	74
3	49	11	375*	7	317	310	60	6	263	266	53	1	321	313	51	1	136	140	65		13,	3, 1	
4	392	391	95	8	285	278	63	7	71	69	116	2	604	619	67	2	500	525	56	0	463	476	59
5	93	104	222*	9	229	215	71	8	204	193	62	3	184	182	55	3	92	107	94	1	152	150	67
6	323	304	149		9,	9, 1		9	49	53	296*	4	426	434	53	4	298	301	51	2	466	470	56
	8,	14, 1		0	372	363	75	10	266	247	89	5	25	4	534*	5	37	65	301*	3	136	126	76
0	175	188	157	1	49	33	197*		10,	6, 1		6	411	404	58	6	99	128	91	4	184	171	64
1	90	54	319*	2	419	409	72	0	712	727	76	7	114	110	87	7	20	22	452*	5	121	117	131
	9,	1, 1		3	32	28	282*	1	119	103	96	8	330	320	60	8	122	142	102	6	129	129	84
0	933	923	102	4	325	325	61	2	670	677	83	9	104	89	119	9	65	64	195*	7	166	169	79
1	262	253	42	5	57	50	188*	3	162	151	66		11,	5, 1			12,	4, 1		8	225	210	78
2	748	756	70	6	456	451	69	4	502	495	98	0	595	594	76	0	444	446	58		13,	5, 1	
3	25	16	265*	7	189	170	74	5	31	24	318*	1	442	442	57	1	230	220	56	0	293	288	63
4	570	577	59	8	235	228	71	6	465	456	69	2	350	352	54	2	431	425	58	1	257	260	60
5	326	315	55		9,	11, 1		7	32	62	325*	3	448	447	58	3	60	71	156*	2	326	320	58
6	165	153	51	0	261	267	88	8	391	377	70	4	265	268	77	4	550	562	61	3	136	123	82
7	138	147	65	1	161	145	189	9	64	69	206*	5	91	51	109	5	60	105	229*	4	445	432	73
8	313	299	61	2	145	174	131		10,	8, 1		6	205	207	71	6	543	545	67	5	30	20	522*
9	46	5	199*	3	73	84	248*	0	206	198	74	7	35	13	301*	7	113	104	94	6	360	347	70

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
13, 5, 1				0	313	336	72	3	133	142	86	0	345	363	54	2	190	213	71	4	20	44	606*
7	23	12	601*	2	269	267	75	4	144	135	90	1	65	5	151*	3	180	174	77	16, 4, 1			
13, 7, 1				4	312	317	81	5	107	117	157	2	268	256	58	4	204	218	103	0	383	379	64
0	307	324	96	6	52	95	247*	6	229	224	69	3	105	119	105	15, 7, 1				1	86	23	148
1	195	196	89	14, 2, 1				14, 6, 1				4	245	240	63	0	246	258	84	2	332	334	61
2	274	259	68	0	428	438	55	0	425	420	70	5	129	107	118	1	86	84	179*	3	13	15	936*
3	203	203	116	1	201	208	57	1	31	24	410*	6	162	159	82	2	266	256	86	16, 6, 1			
4	162	179	139	2	433	428	56	2	469	460	72	15, 3, 1				16, 0, 1				0	119	125	140
5	65	76	207*	3	25	54	374*	3	59	29	260*	0	178	180	69	0	426	443	81	1	36	17	363*
6	172	182	111	4	335	343	57	4	306	296	87	1	35	10	288*	2	315	307	83	17, 1, 1			
13, 9, 1				5	35	46	355*	5	50	53	260*	2	233	236	60	4	432	418	88	0	278	280	65
0	160	162	153	6	318	308	62	14, 8, 1				3	70	69	160*	16, 2, 1				1	244	247	64
1	79	67	290*	7	40	5	279*	0	20	20	984*	4	234	223	66	0	53	37	206*	2	197	195	75
2	229	233	151	14, 4, 1				1	45	10	334*	5	172	154	122	1	15	51	684*	17, 3, 1			
3	28	34	742*	0	140	143	88	2	93	61	242*	15, 5, 1				2	72	78	160*	0	20	63	586*
4	126	134	137	1	141	139	84	3	63	49	336*	0	240	245	73	3	56	11	215*	1	133	133	103
14, 0, 1				2	43	47	221*	15, 1, 1				1	75	43	174*								

Appendix E
Mass Spectrum

Appendix E
Mass Spectrum

JUL-03-2002 WED 04:01 PM CSU CHEMISTRY DEPT FAX NO. 9704911801 P. 02

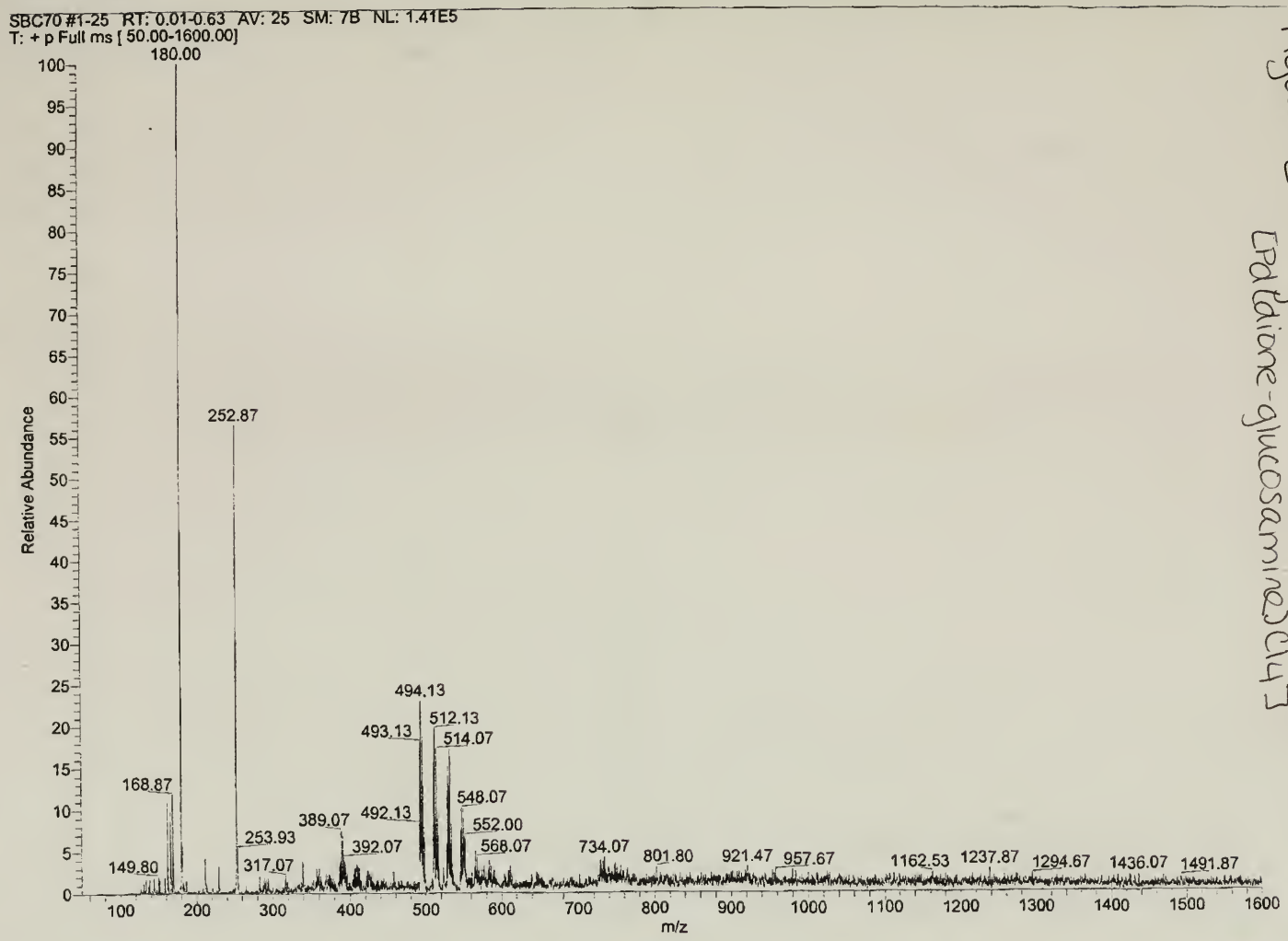

Figure E1: High Resolution Mass Spec of Pd dione-glucosamine Cl4

E1

JUL-03-2002 WED 04:01 PM CSU CHEMISTRY DEPT FAX NO. 9704911801 P. 03

SBC70 #1-25 RT: 0.01-0.63 AV: 25 SM: 7B NL: 1.41E5
T: + p Full ms [50.00-1600.00]

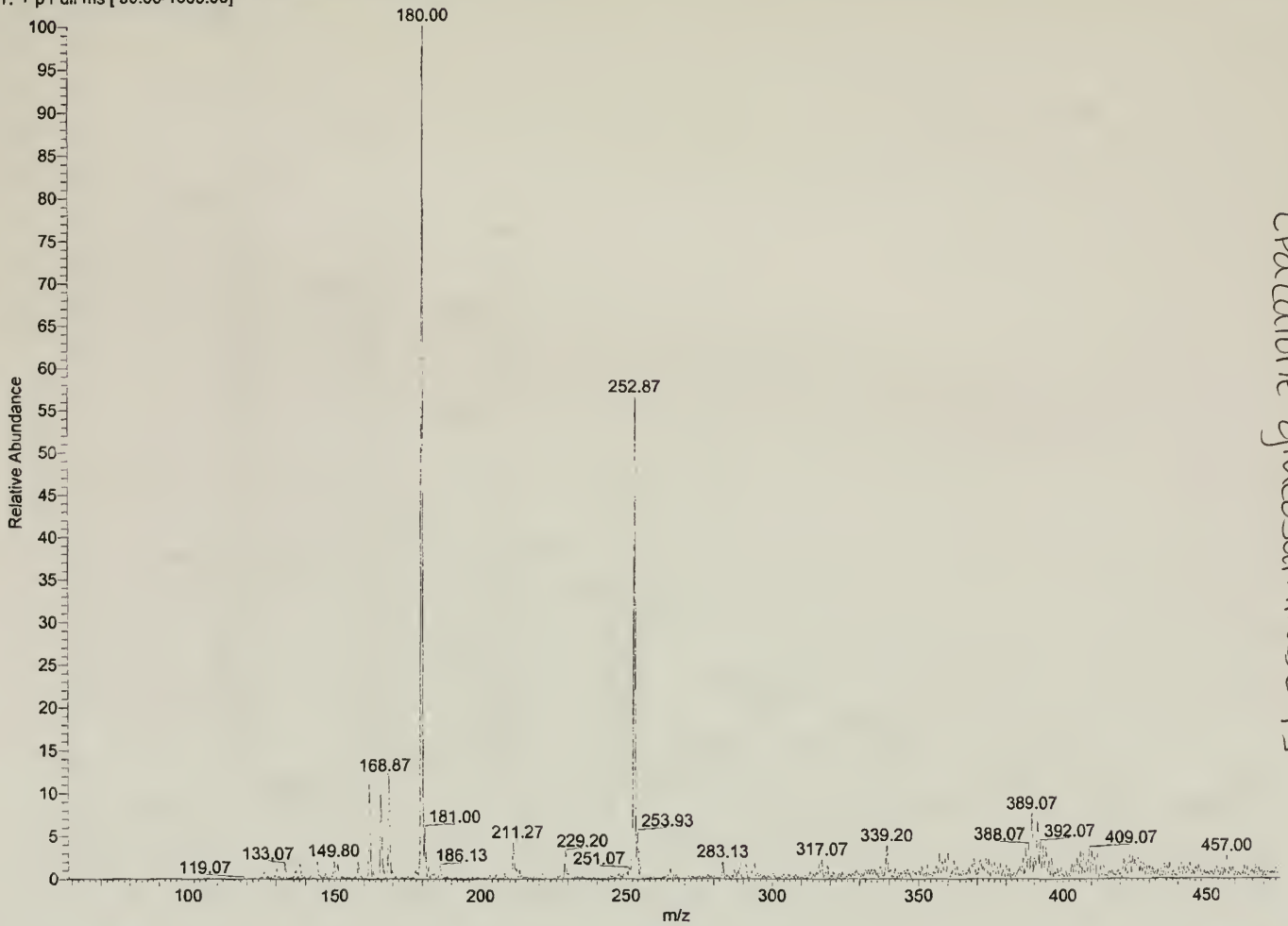

Figure E2: High Resolution Mass Spec of [Pd(dione-glucosamine)Cl4]

E2

SBC70 #1-25 RT: 0.01-0.63 AV: 25 SM: 7B NL: 3.24E4
T: + p Full ms [50.00-1600.00]

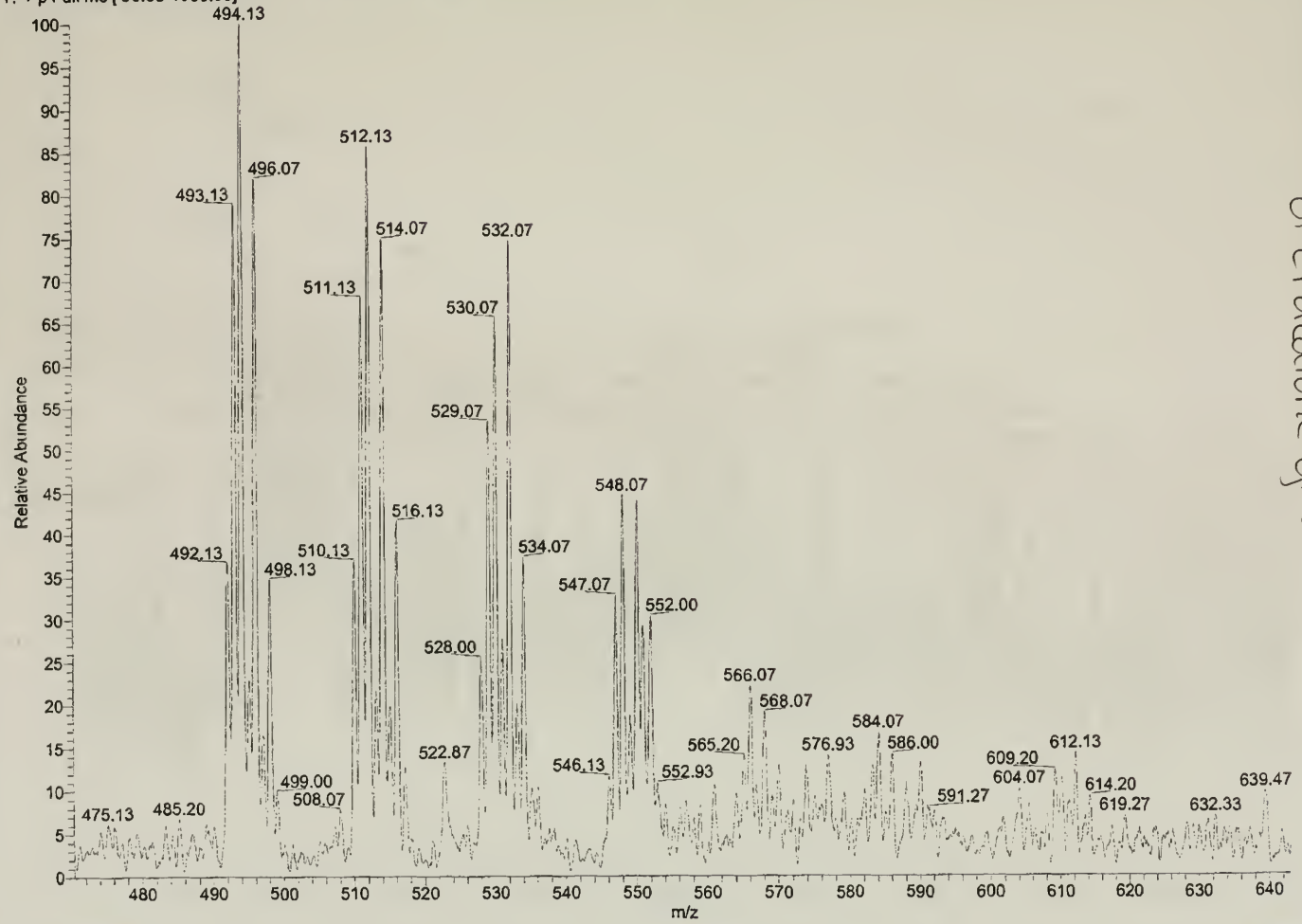

Figure E3: High Resolution Mass Spec of EPAdione-glucosamine[C14]

E3

SBC70 #1-25 RT: 0.01-0.63 AV: 25 SM: 7B NL: 5.95E3
T: + p Full ms [50.00-1600.00]

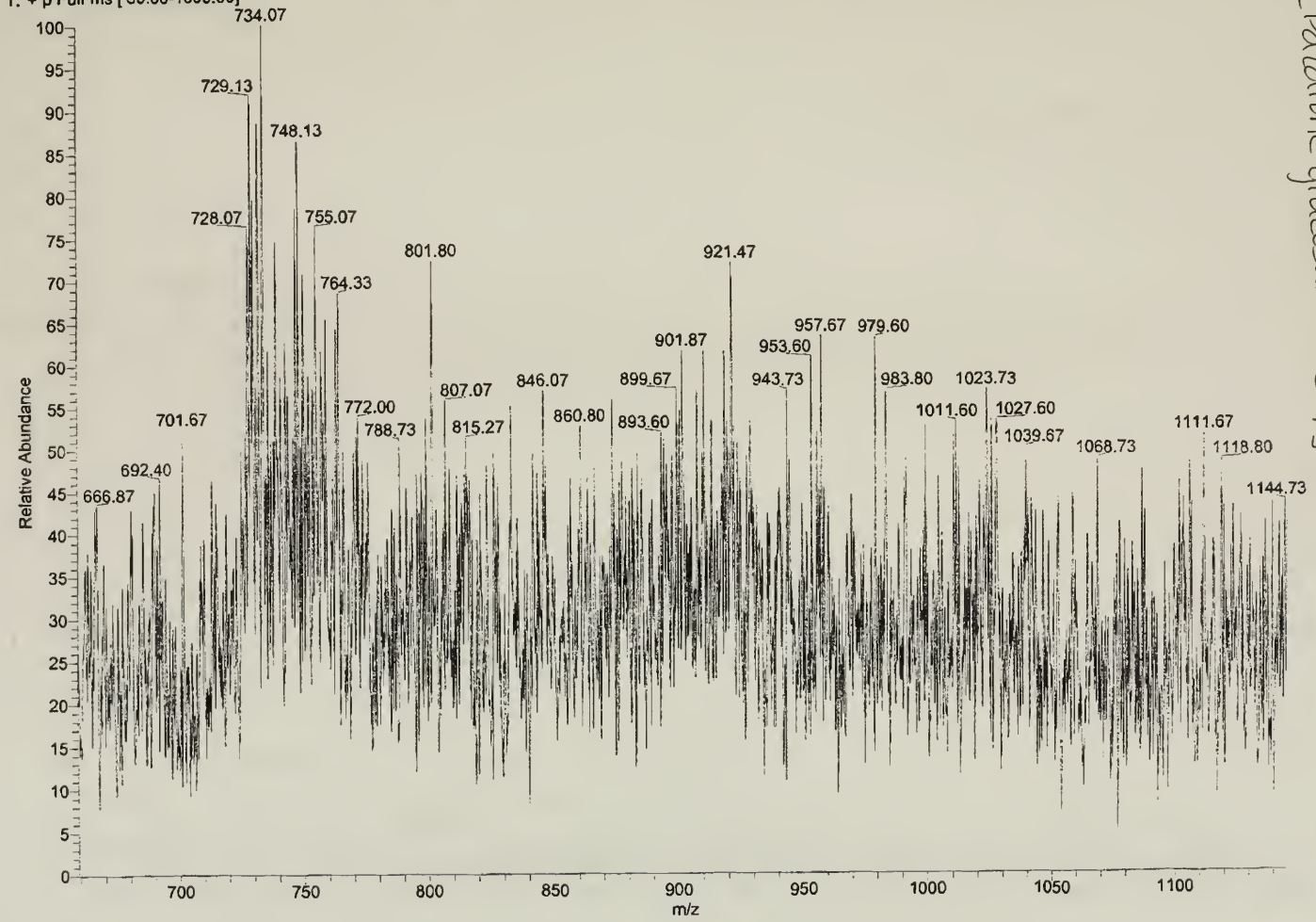

Figure E4: High Resolution Mass Spec of Pd(dione-glucosamine)Cl4

E4

JUL-03-2002 WED 04:02 PM CSU CHEMISTRY DEPT FAX NO. 9704911801 P. 05

JUL-03-2002 WED 04:09 PM CSU CHEMISTRY DEPT FAX NO. 9704911801 P. 19

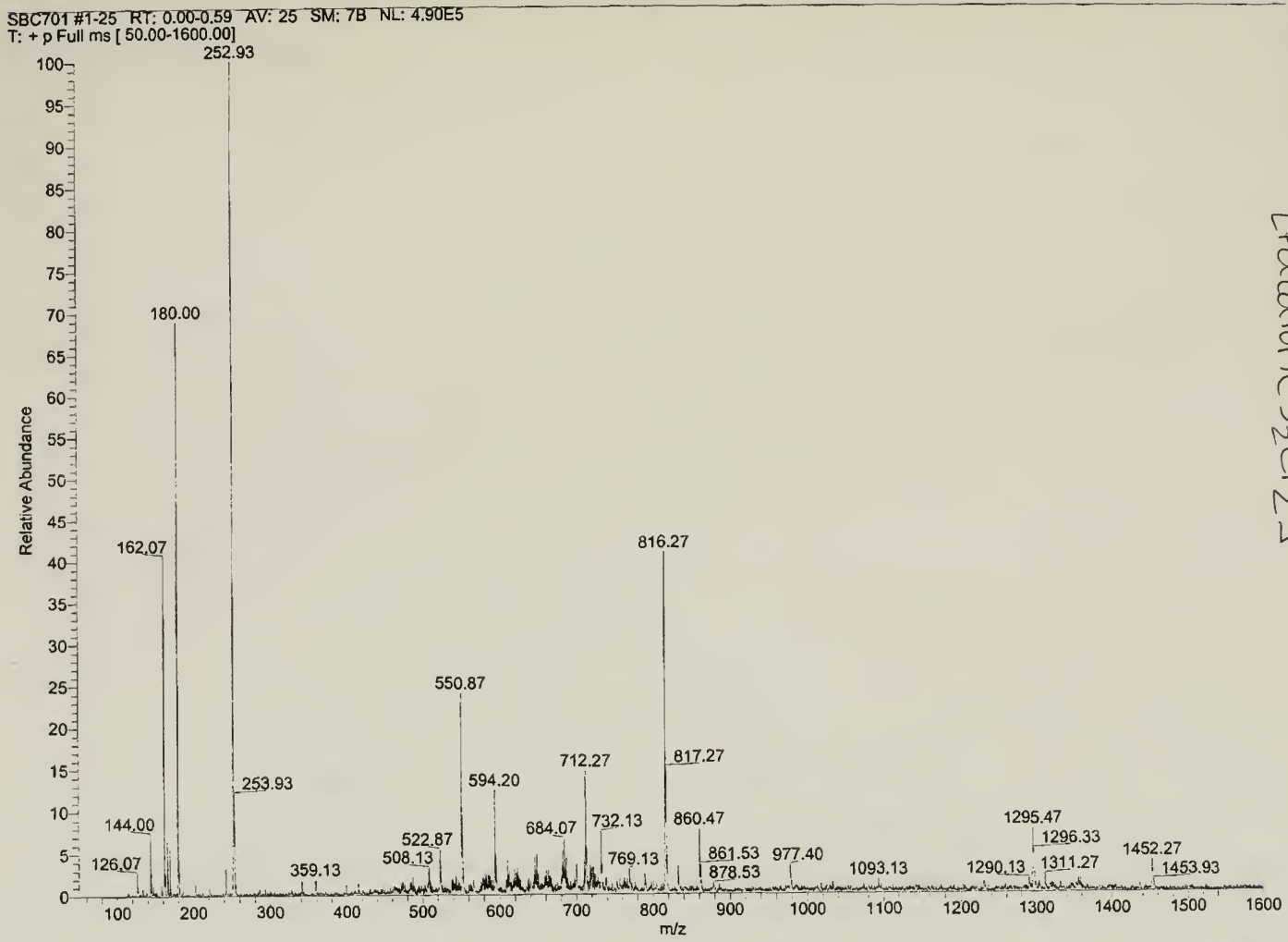

Figure E5: High Resolution Mass Spec of [Pd(dione)$_2$Cl$_2$]

E5

JUL-03-2002 WED 04:09 PM CSU CHEMISTRY DEPT FAX NO. 9704911801 P. 20

SBC701 #1-25 RT: 0.00-0.59 AV: 25 SM: 7B NL: 4.90E5
T: + p Full ms [50.00-1600.00]

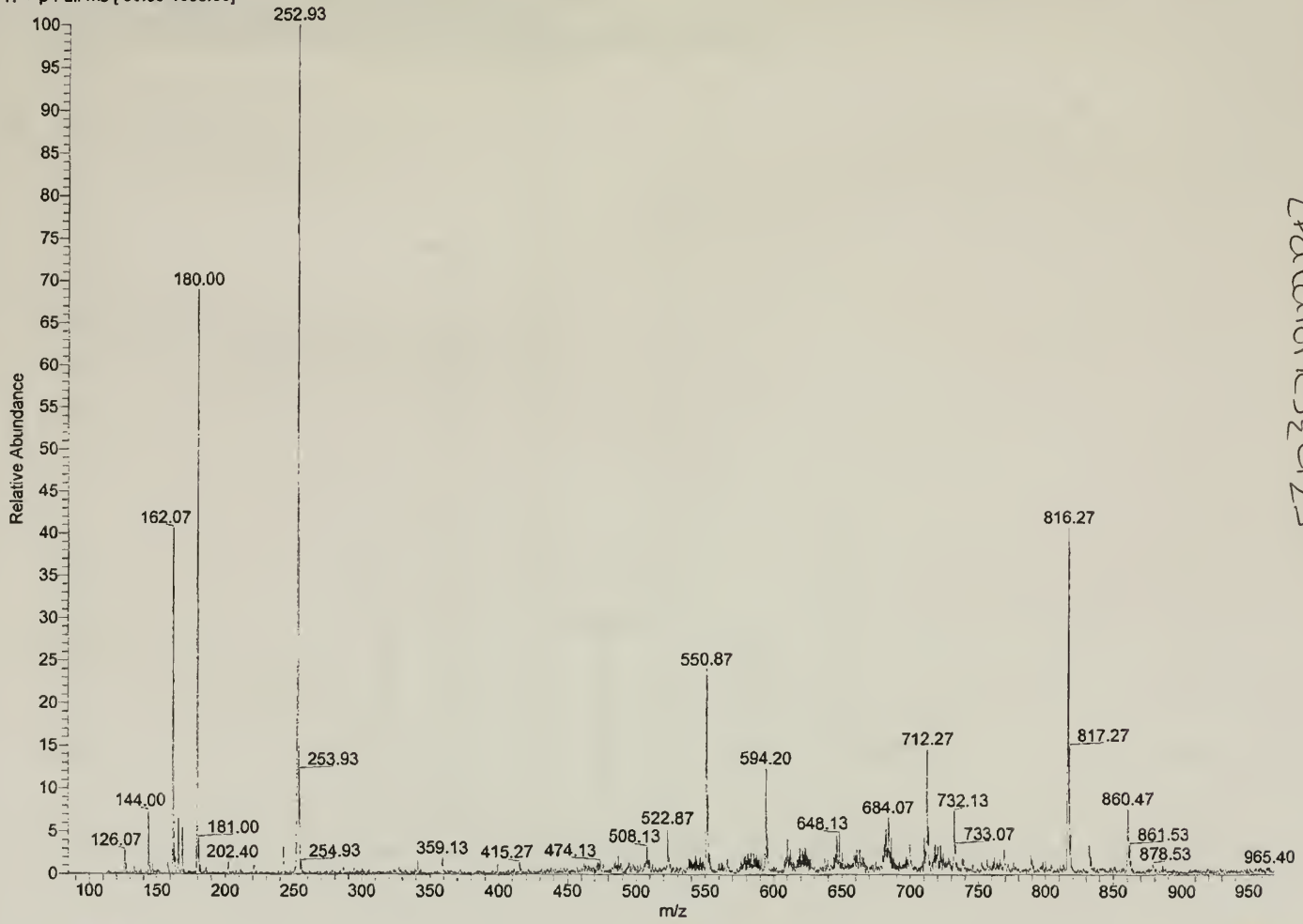

Figure E6: High Resolution Mass Spec of [Pd(dione)2Cl2]

E6

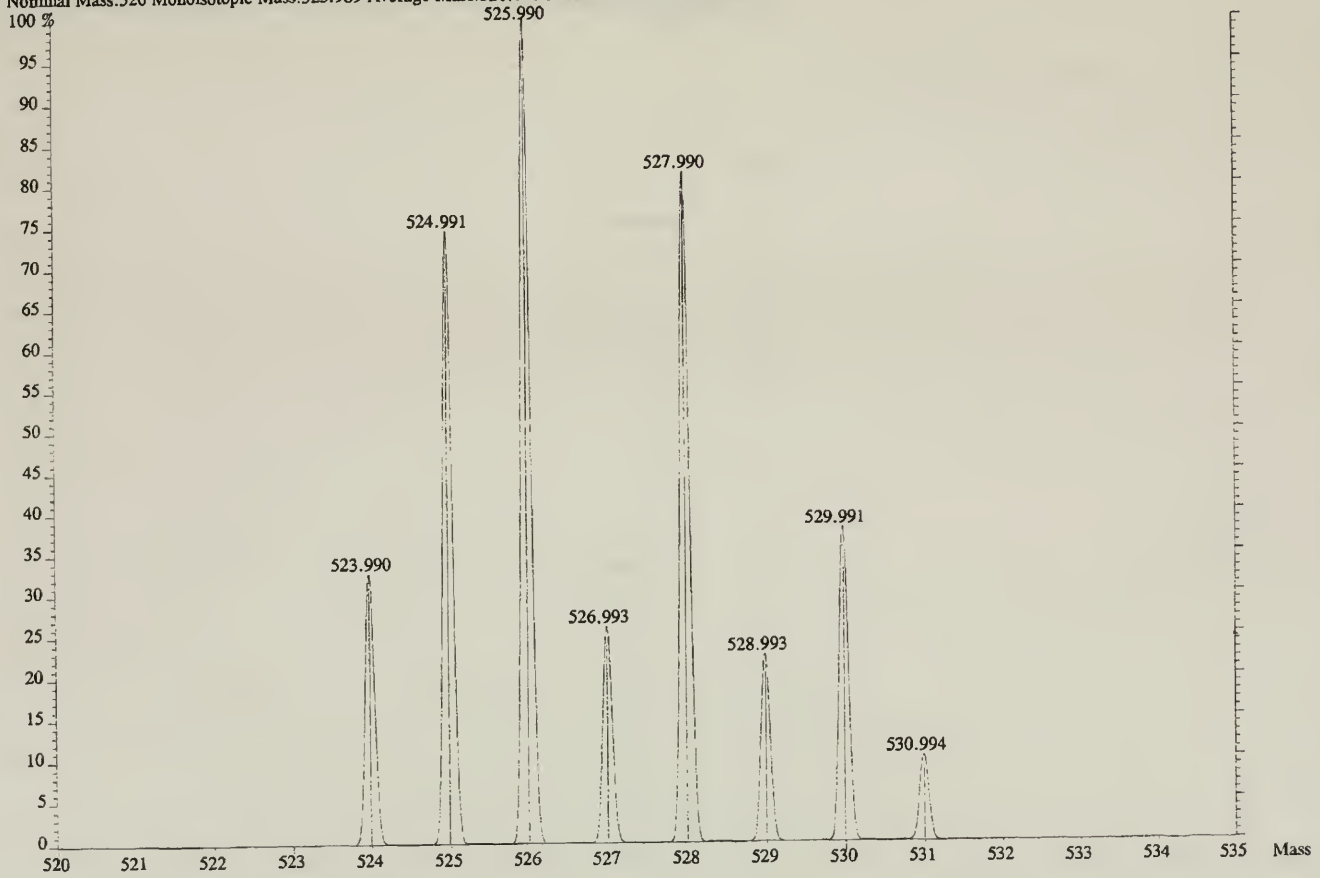

Figure E-7: High Resolution Mass Spec of $[Pd(dione)_2Cl_2]$

E-7

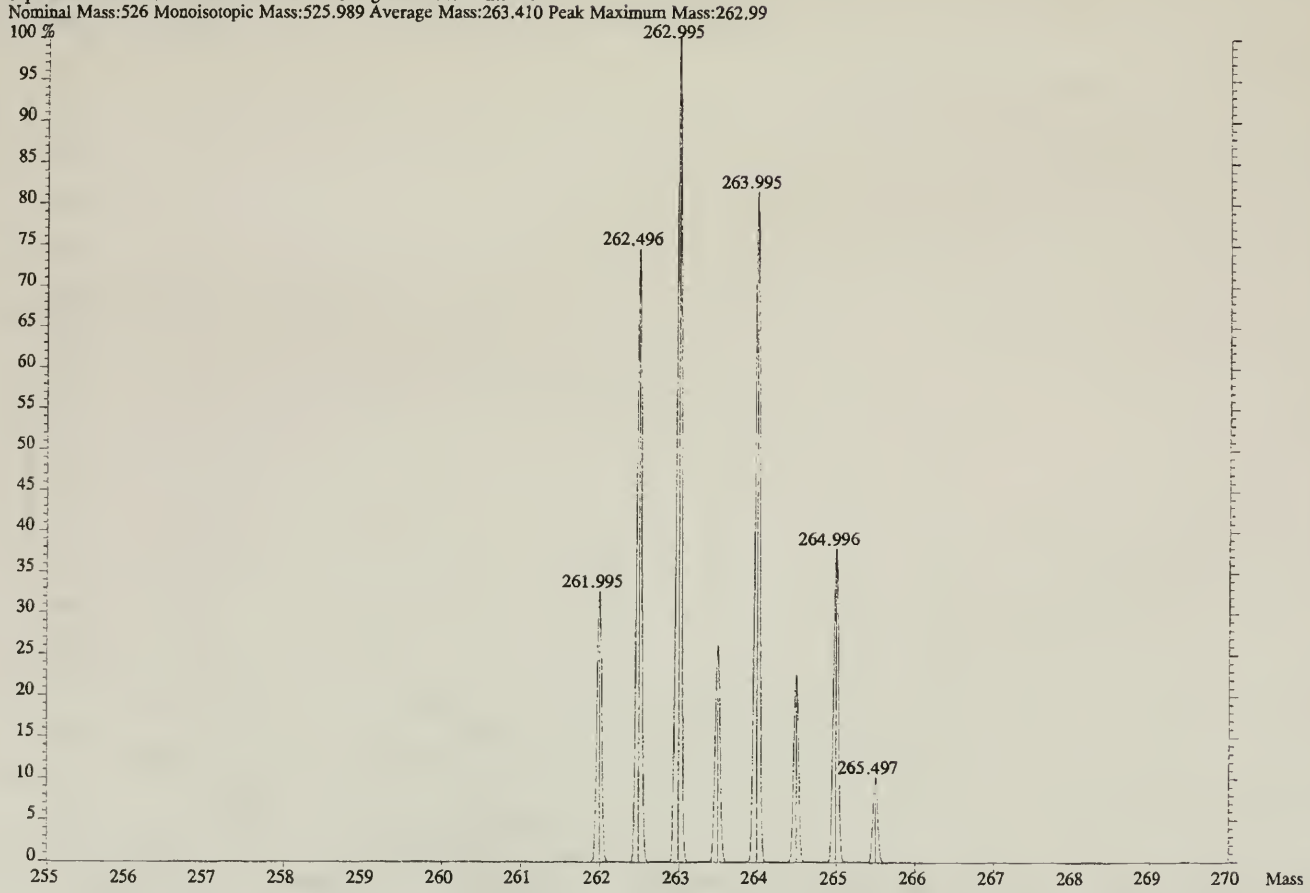

Figure E8: High Resolution Mass Spec of $[Pd(dione)_2Cl_2]$

E8

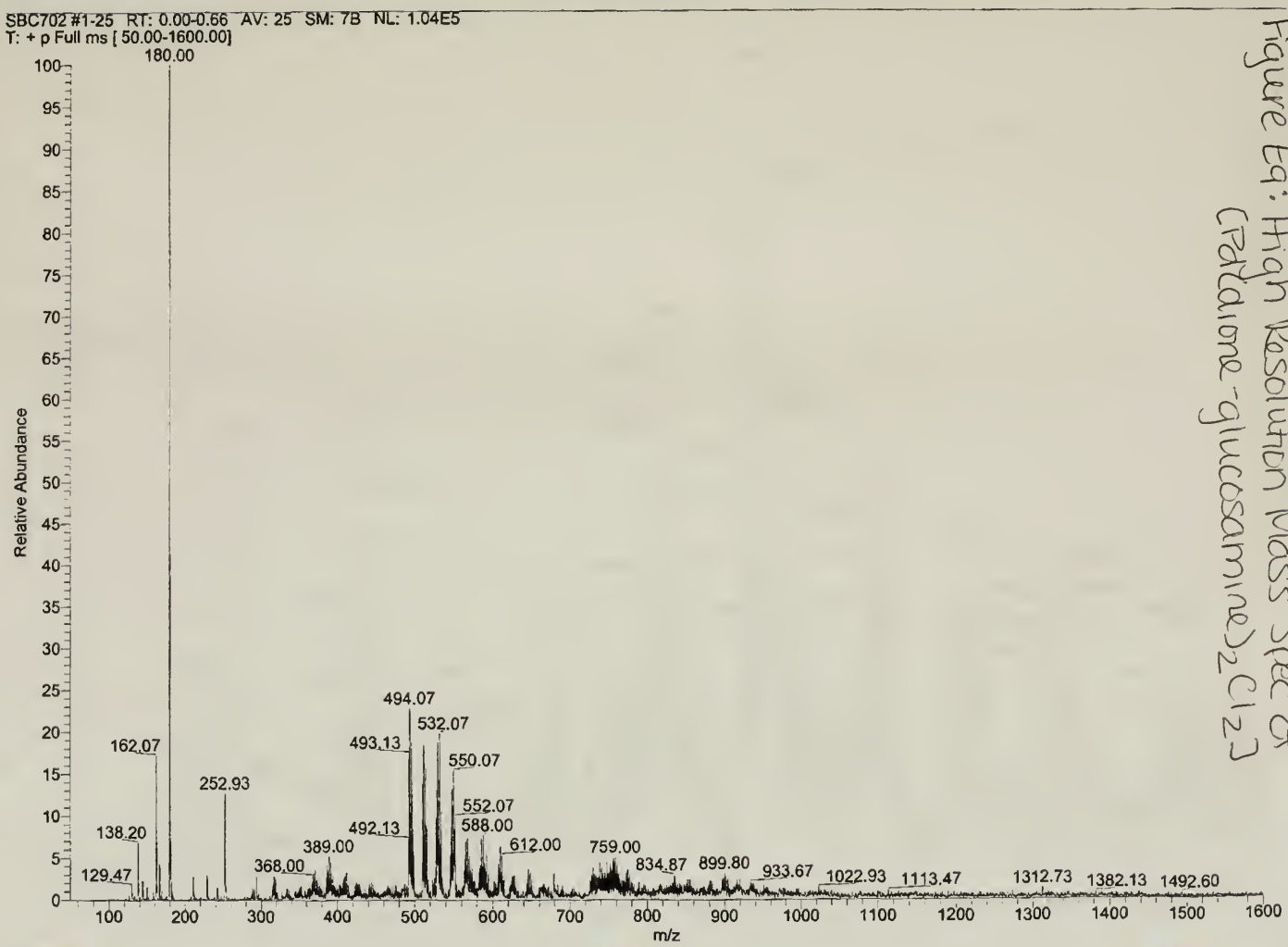

Figure Eq: High Resolution Mass Spec of (Pdione-glucosamine)$_2$Cl$_2$

JUL-03-2002 WED 04:06 PM CSU CHEMISTRY DEPT FAX NO. 9704911801 P. 15

Eq

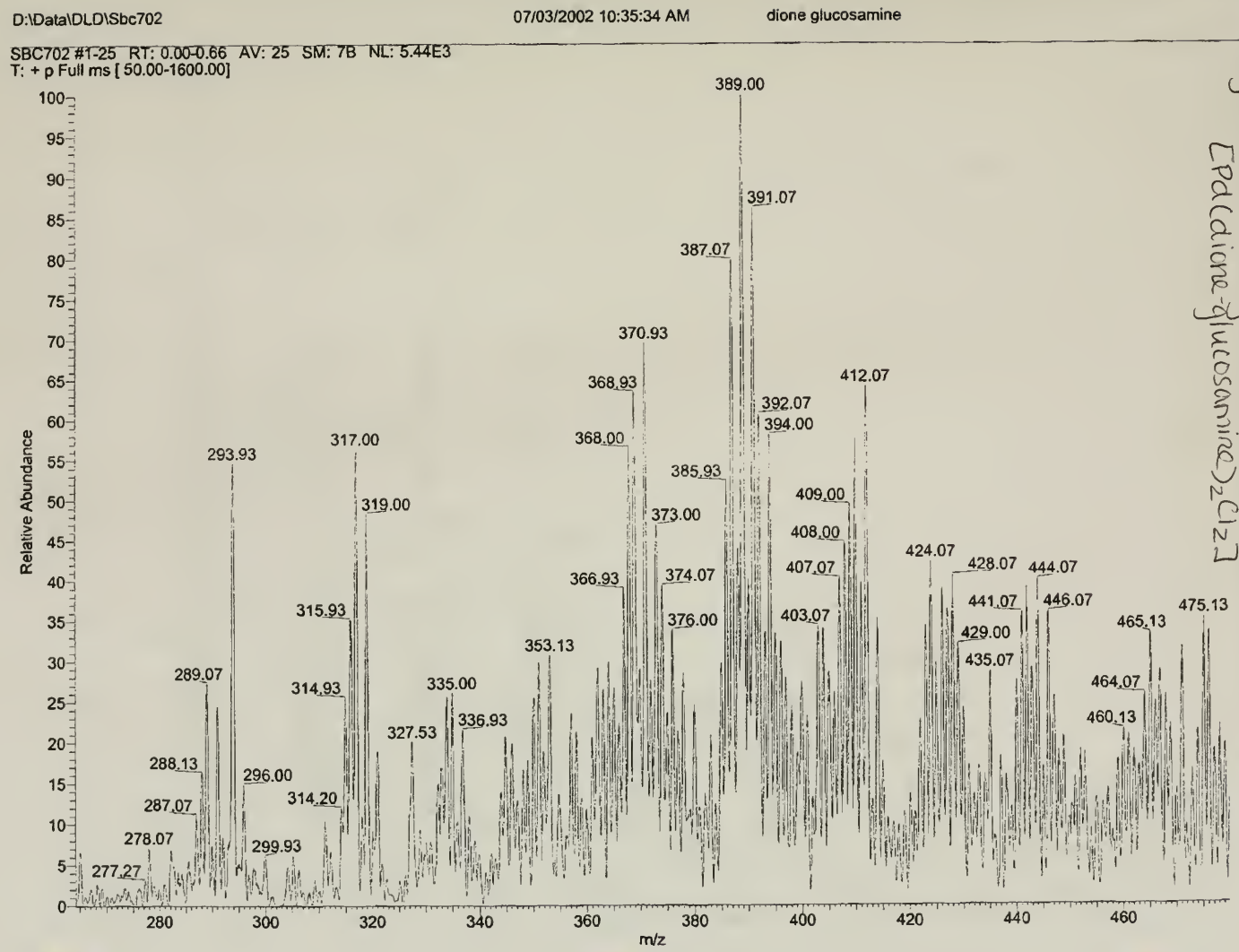

Figure E10: High Resolution Mass Spec of Epaldione-glucosamine)$_2$Cl$_2$

E10

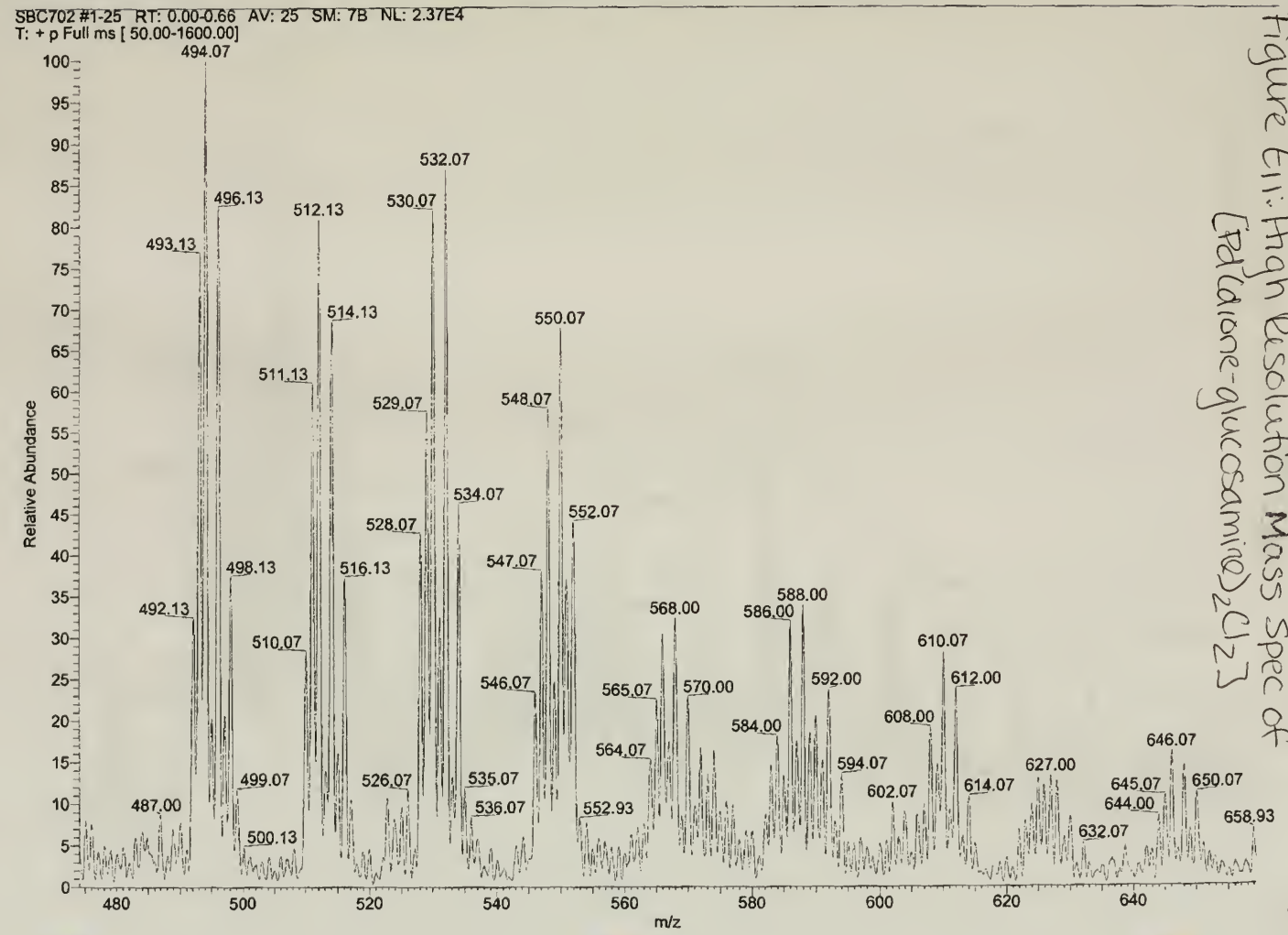

Figure E11: High Resolution Mass Spec of (Pd(dione-glucosamine)2Cl2)

E11

JUL-03-2002 WED 04:07 PM CSU CHEMISTRY DEPT FAX NO. 9704911801 P. 17

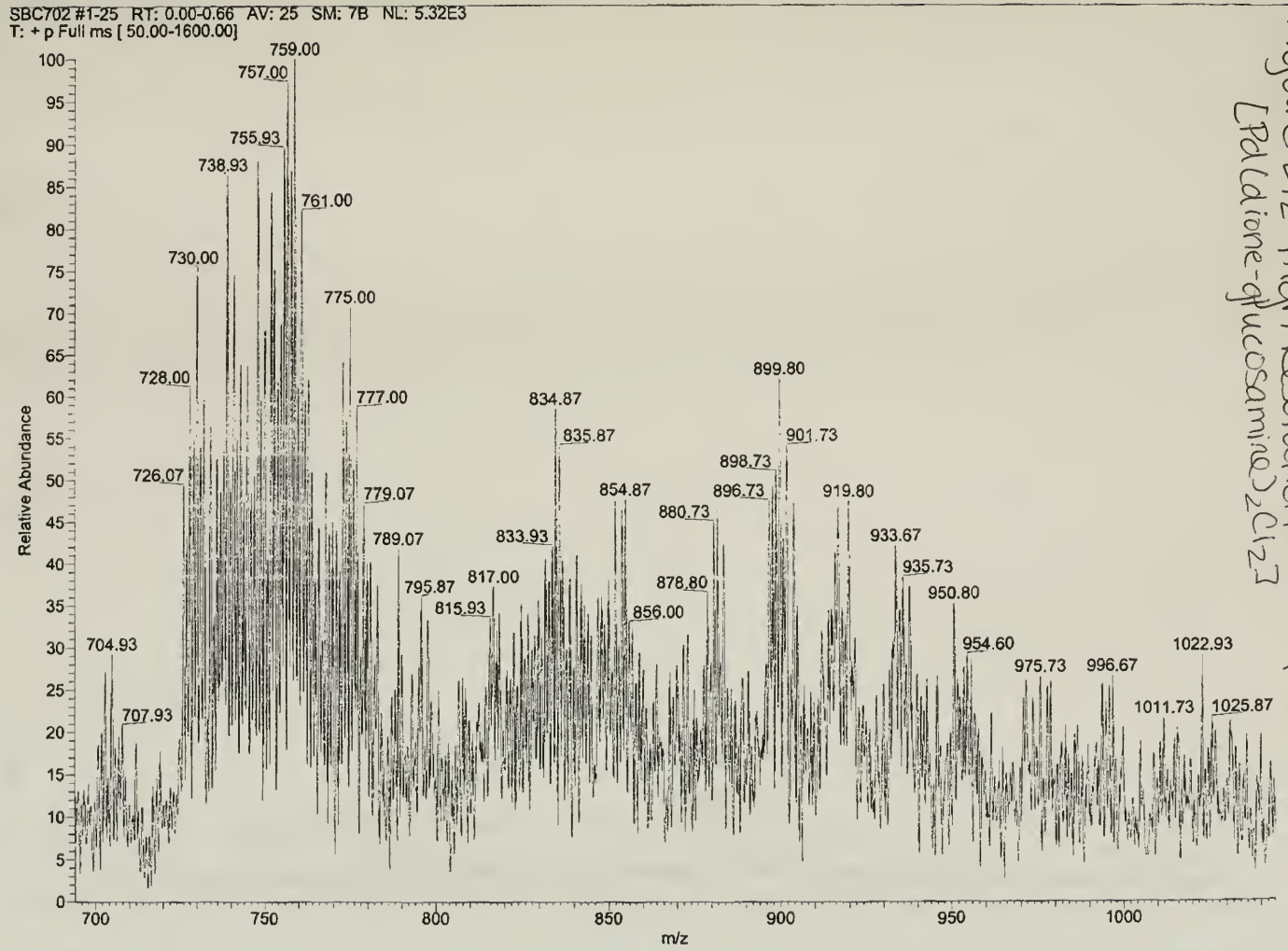

Figure E12: High Resolution Mass Spec of [Pd(dione-glucosamine)2Cl2]

E12

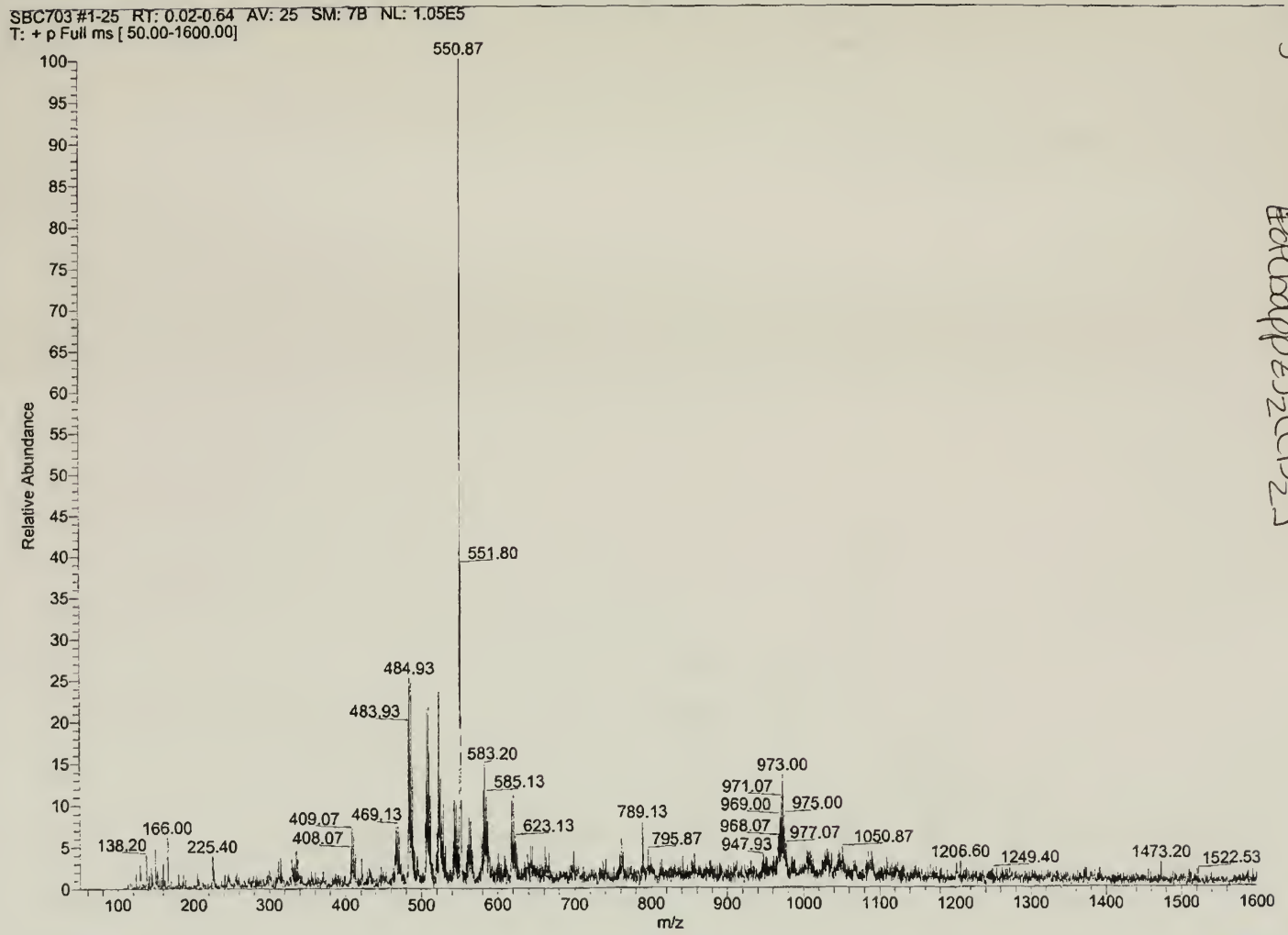

Figure E13: High Resolution Mass Spec of Pd(bdppz)2(Cl)2

E13

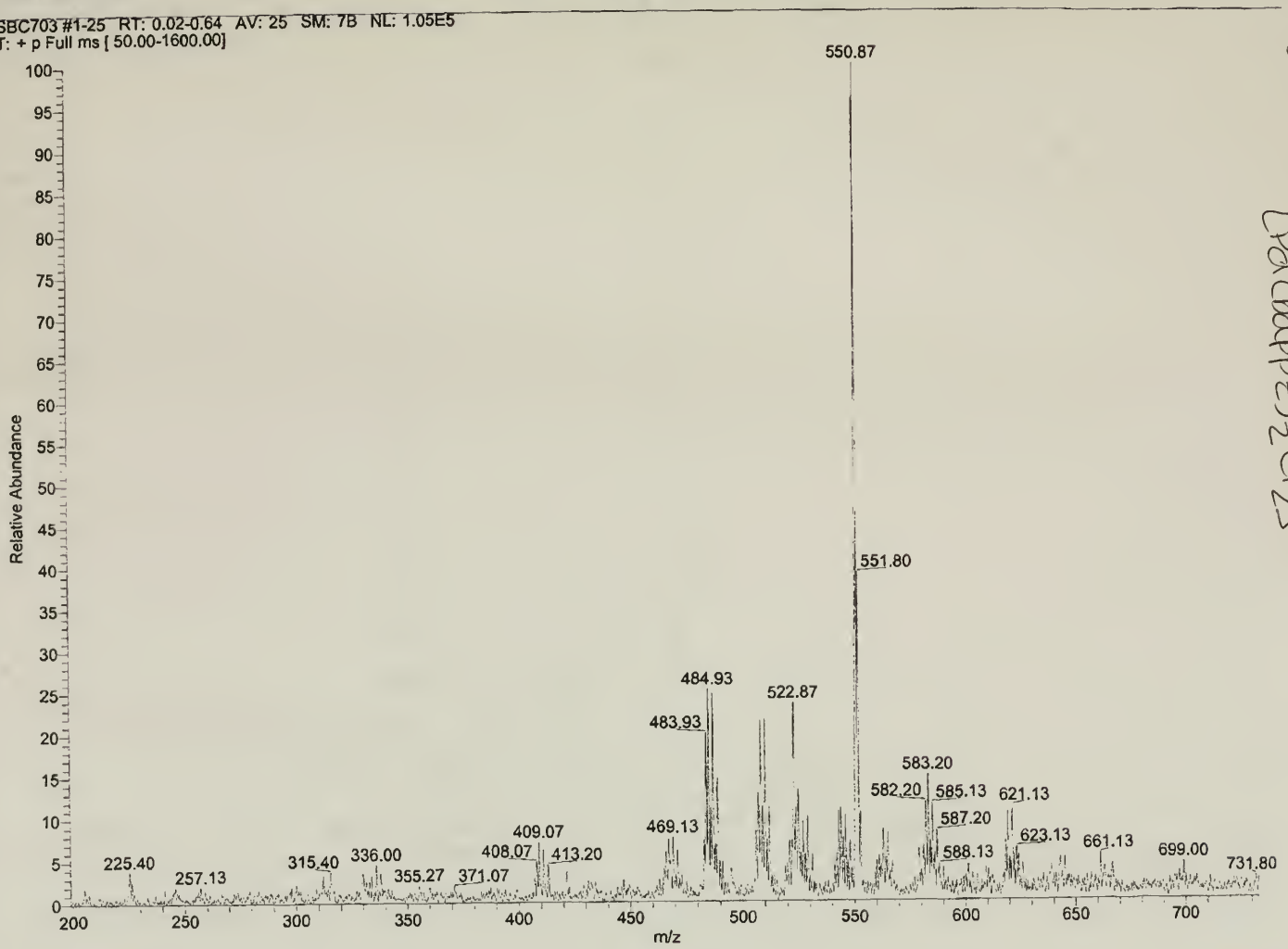

Figure E14: High Resolution Mass Spec of $Pd(bdppz)_2(Cl)_2$

E14

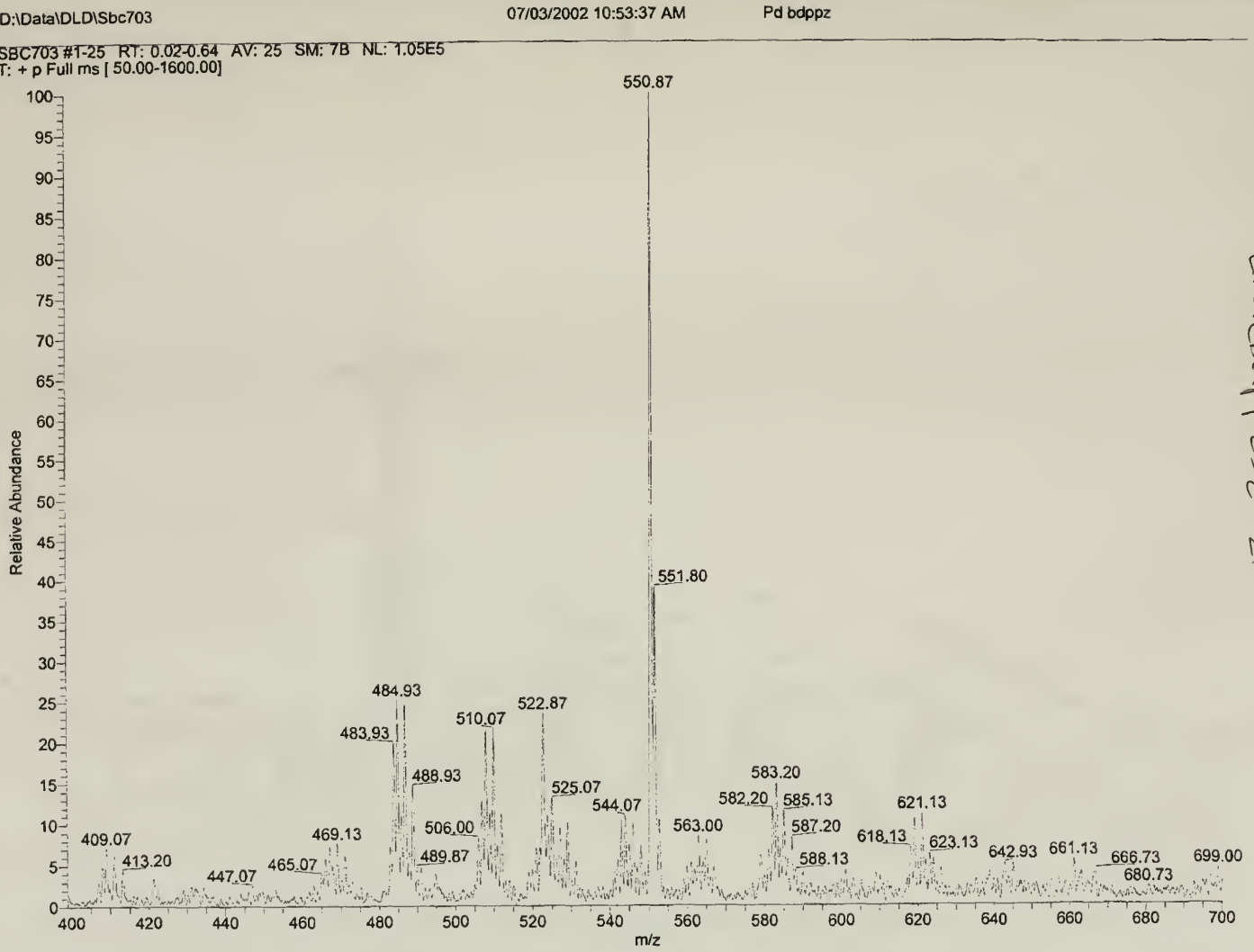

Figure E15: High Resolution Mass Spec of [Pd(bdppz)2Cl2]

E15

SBC703 #1-25 RT: 0.02-0.64 AV: 25 SM: 7B NL: 1.41E4
T: + p Full ms [50.00-1600.00]

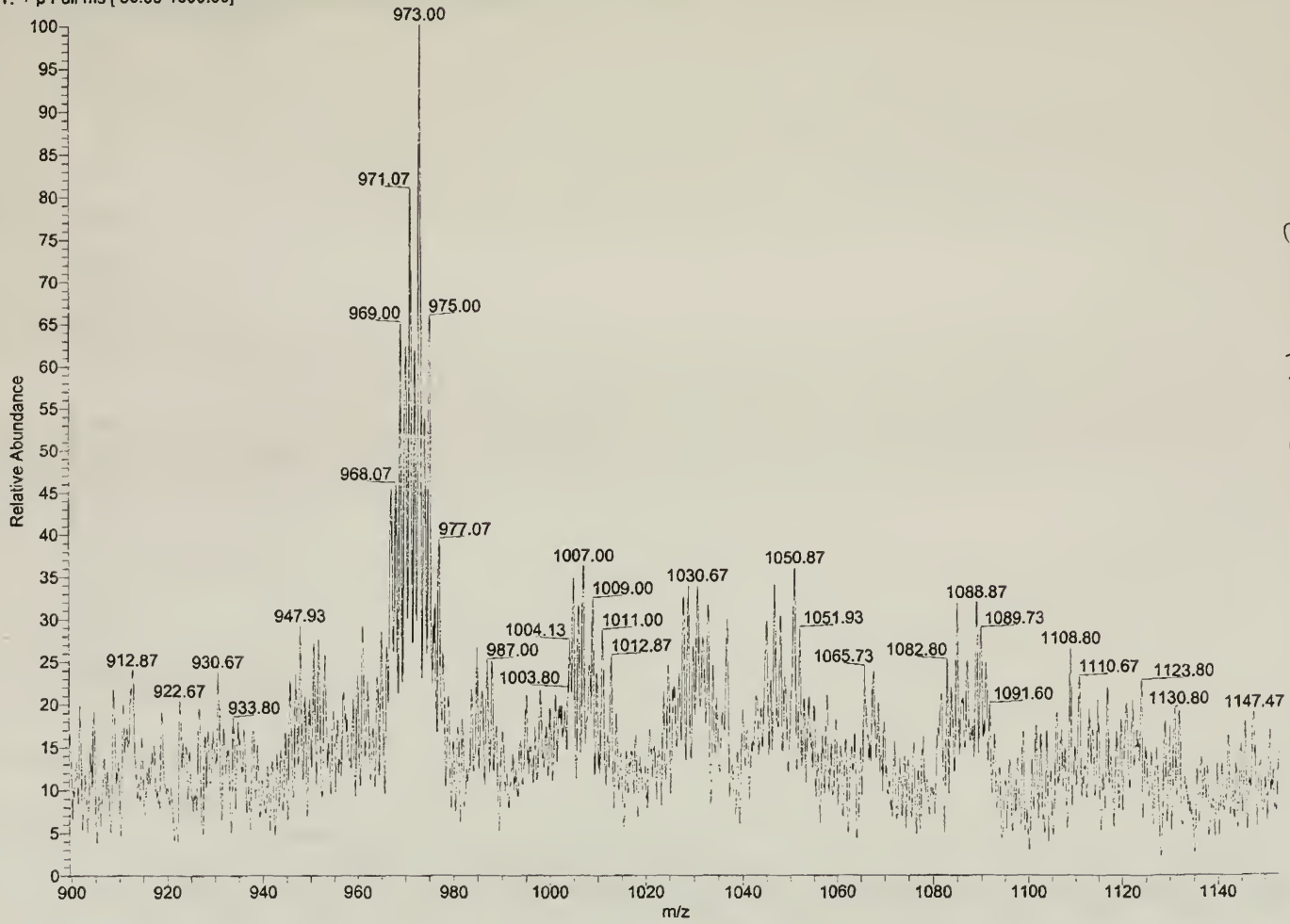

Figure E16: High Resolution Mass Spec of [Pd(bppz)2Cl2]

E16

JUL-03-2002 WED 04:06 PM CSU CHEMISTRY DEPT FAX NO. 9704911801 P. 14

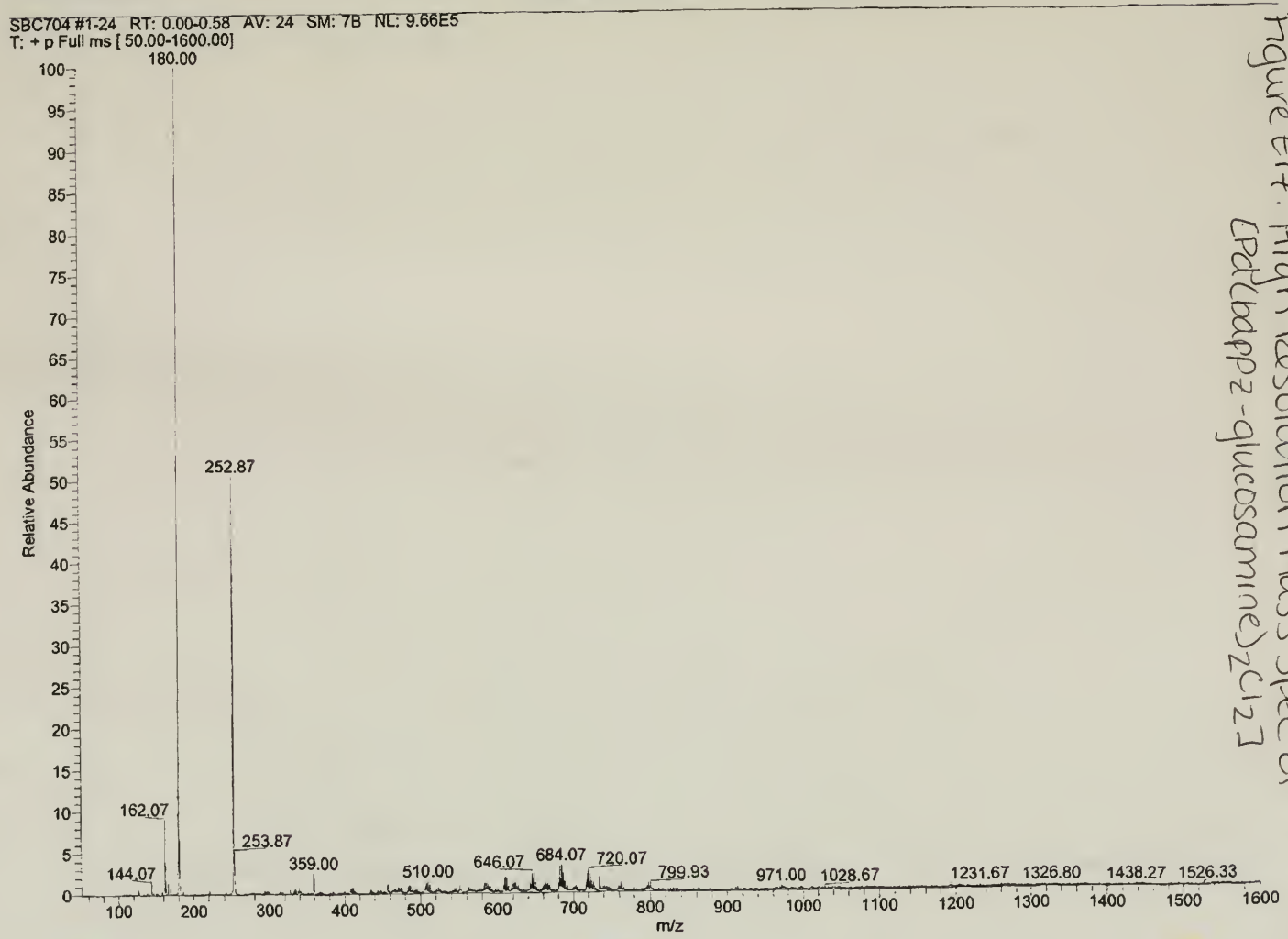

Figure E17: High Resolution Mass Spec of (Pd(bdppz-glucosamine)2Cl2)

E17

SBC704 #1-24 RT: 0.00-0.58 AV: 24 SM: 7B NL: 9.66E5
T: + p Full ms [50.00-1600.00]

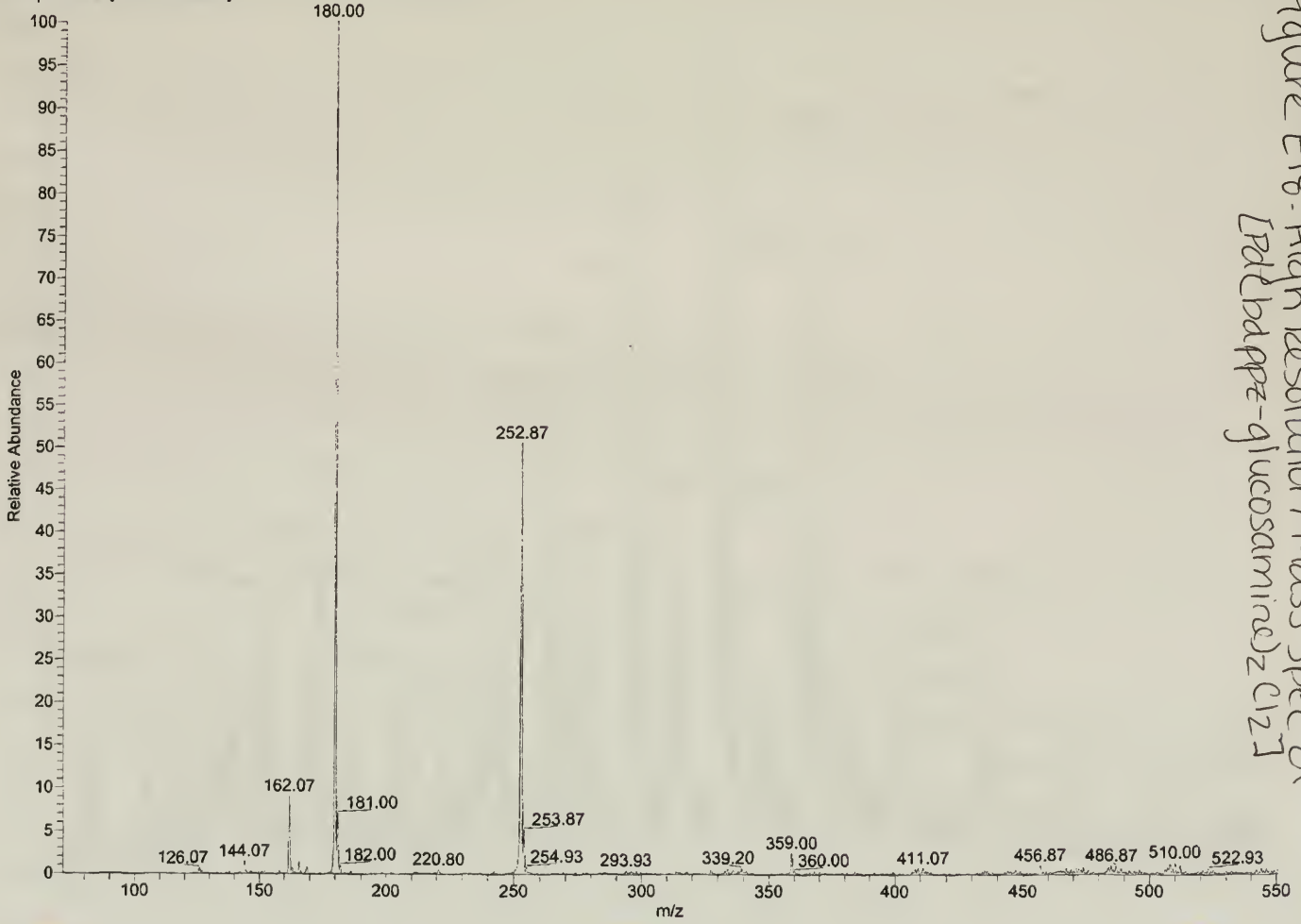

Figure E18: High Resolution Mass Spec of [Pd(bdppz-glucosamine)2 Cl2]

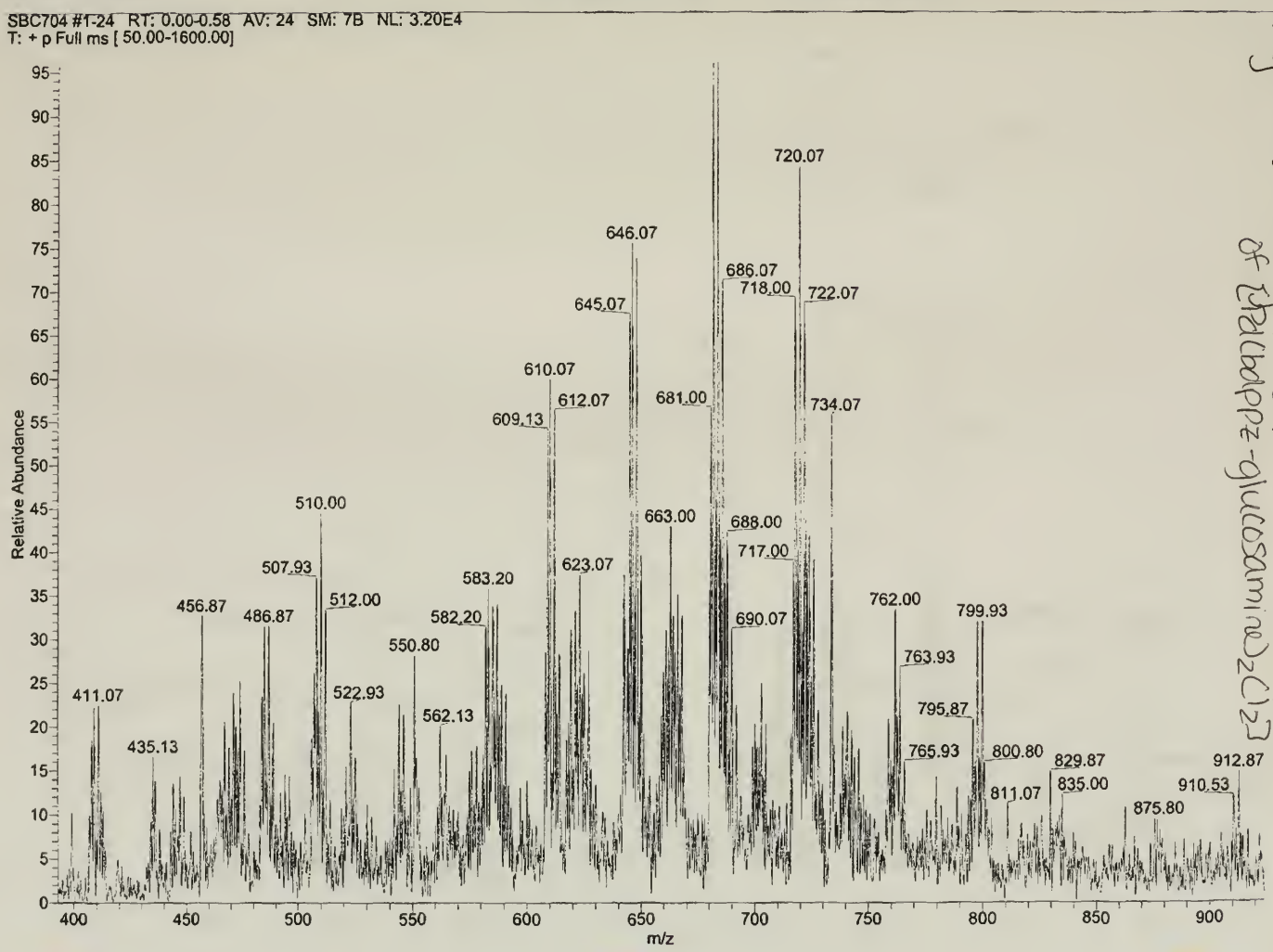

Figure E19: High Resolution Mass Spec of Pd(bdppz-glucosamine)2Cl2

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E19

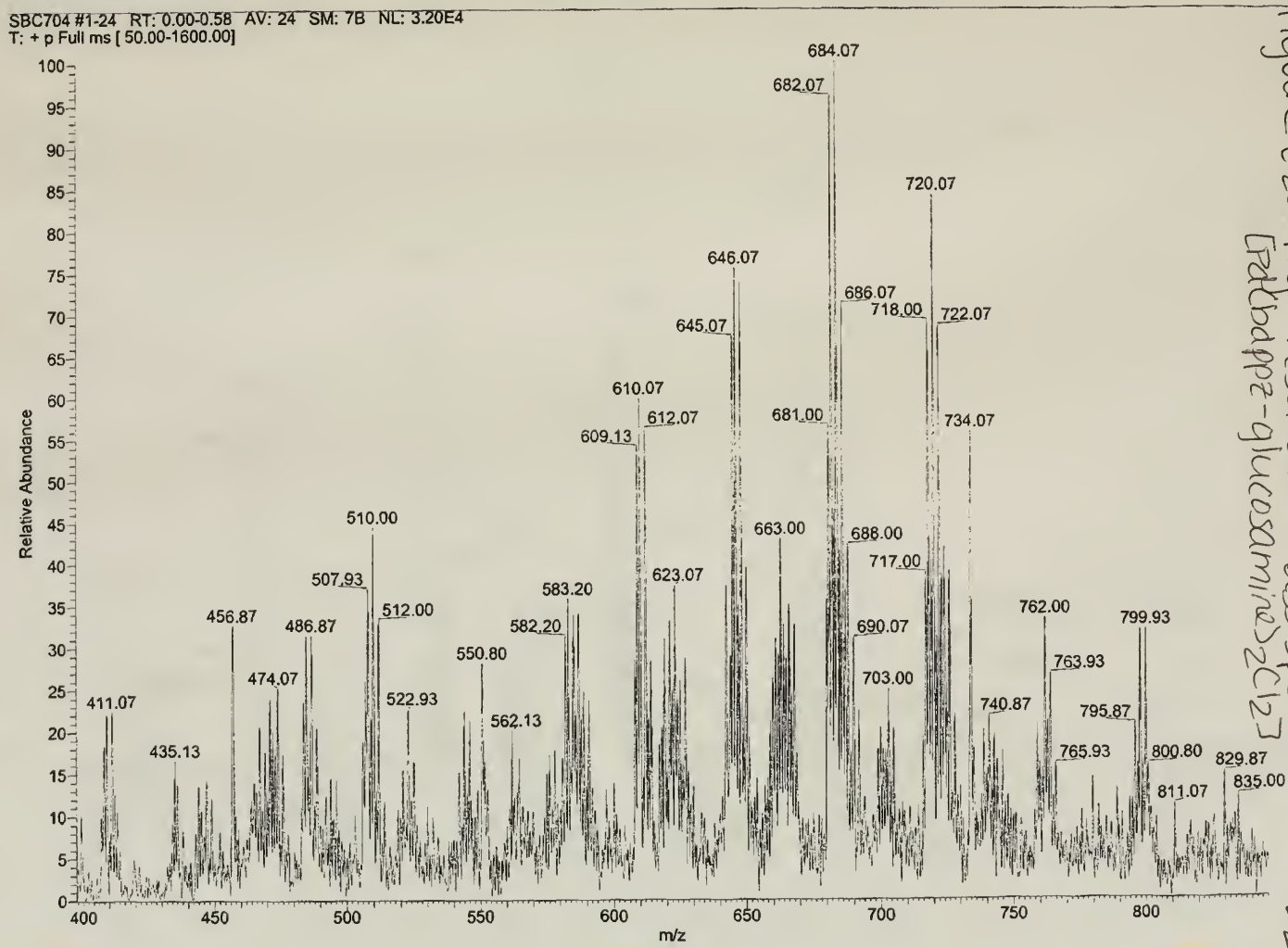

Figure E20: High Resolution Mass Spec of Pd(bdppz-glucosamine)2(Cl2)

E20

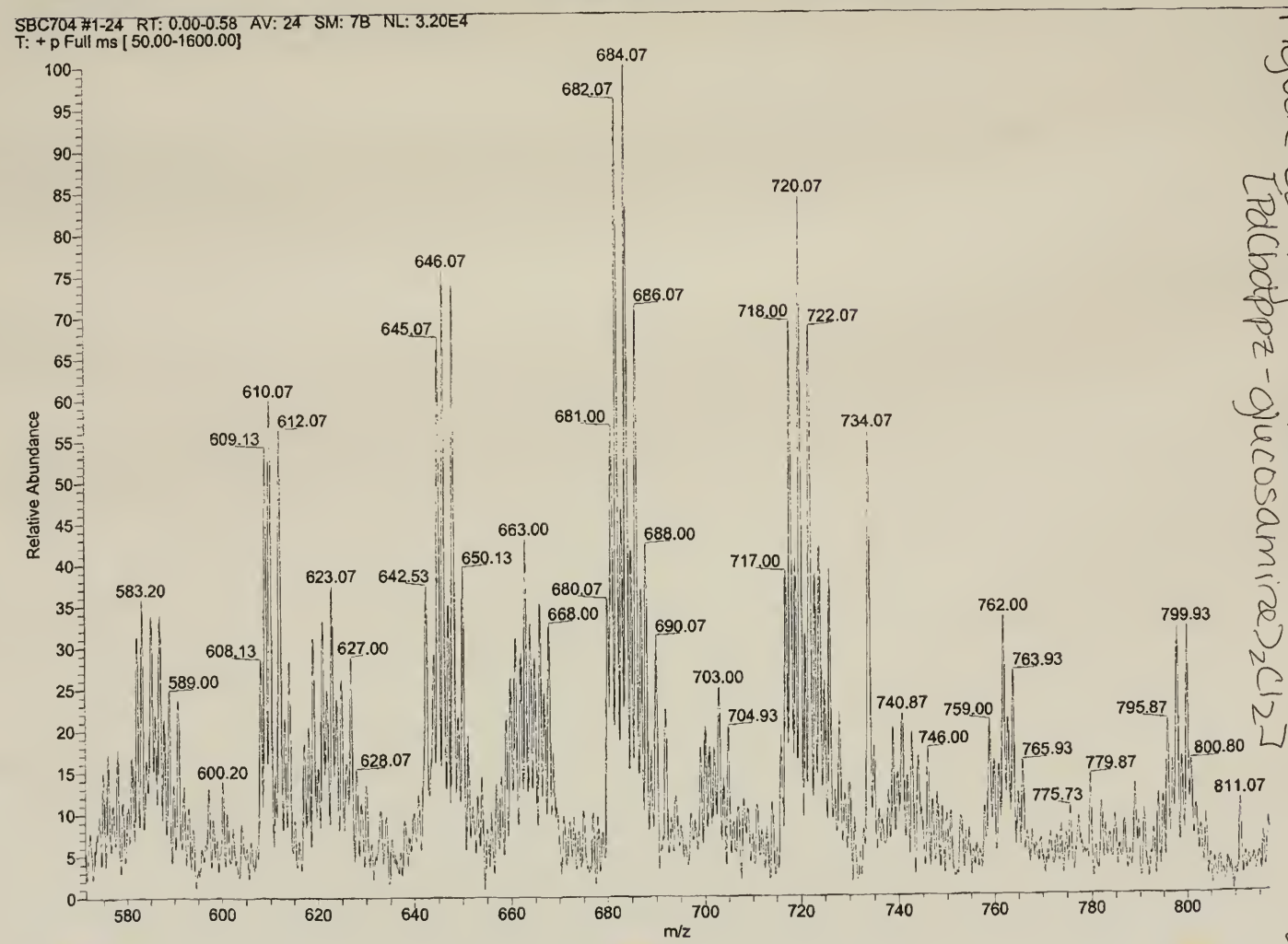

Figure E21: High Resolution Mass Spec of [Pd(bdppz-glucosamine)2Cl2] - E21

Appendix F
Cyclic Voltammogram

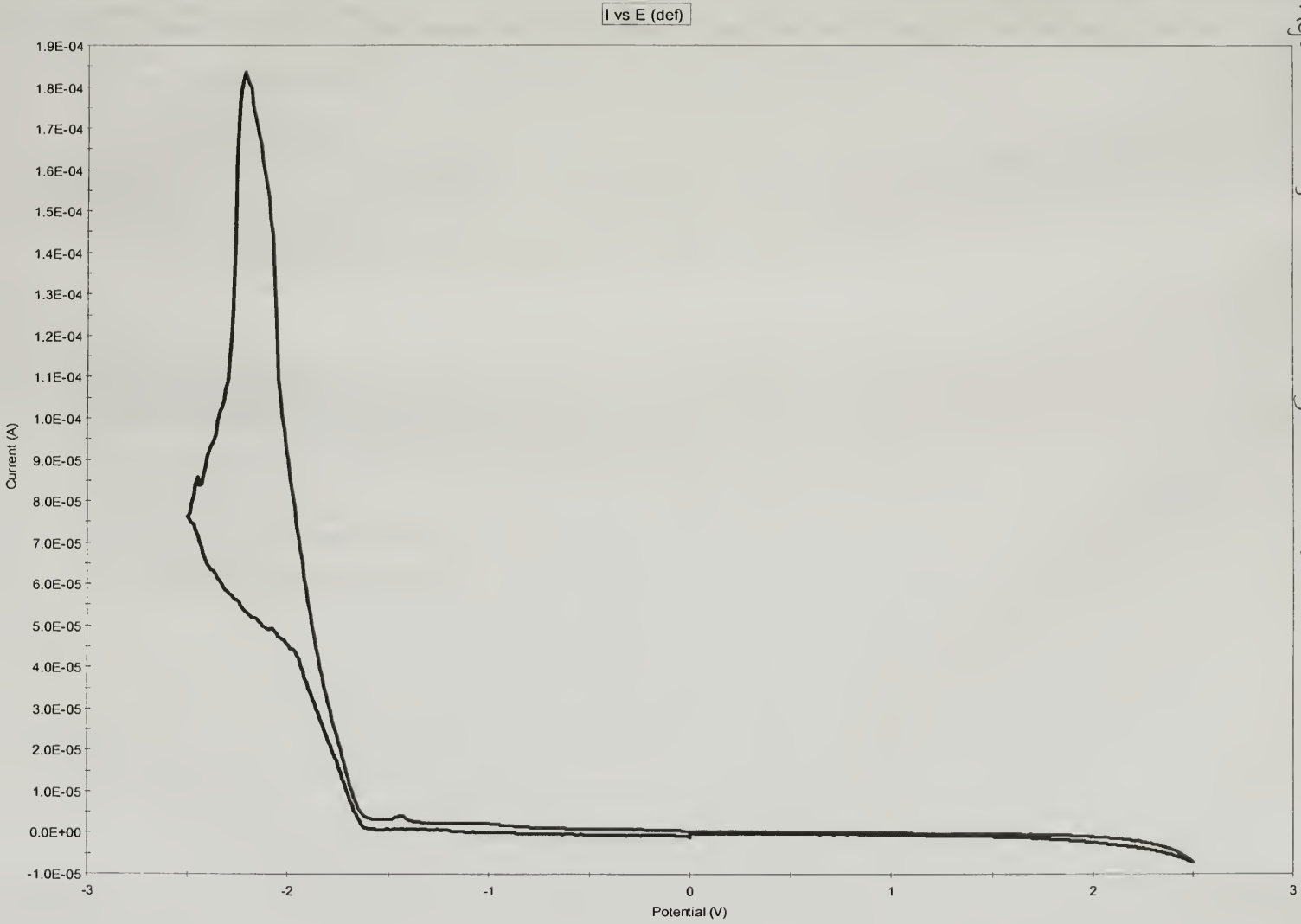

Figure F1: Cyclic voltammogram of [Pt(dione)Cl4]

F1

Experiment Created: 4/7/03 4:51:37 PM
Experiment Description: \A Cyclic Voltammetry template with Two Vertex Potentials. Enter Initial, Vertex1, Vertex2, and Final potentials and Scan Rate.

Cell Definition:
- Potentiostat: 2631 Revision 219, Opt 91
- Analyzer: None
- Background Dataset: None
- Working Electrode: Solid Electrode
- Working Electrode Area: 1.000 cm^2
- Reference Electrode: Ag, AgCl / KCl (3.5 M) (0.205 V)

Scan Definition:
- Initial Potential: 0.0000000 V vs ref
- Vertex Potential: 2.5000000 V vs ref
- Vertex Potential: -2.5000000 V vs ref
- Final Potential: 0.0000000 V vs ref
- Scan rate: 25.00474 mV/s

PreScan Definition:
- Purge Time: disabled
- Condition Time: disabled
- Condition Potential: disabled
- Open circuit: -0.066 V (Measured)
- Deposition Time: disabled
- Equilibration Time: 15 sec

Options:
- Current Ranging: Automatic
- Rise Time: Automatic
- I Signal Conditioning: Automatic
- Ignore external WAIT line in: YES
- Issue trigger out before starting experiment: NO
- Sample auxilary input: NO
- Reset potentiostat before starting experiment: YES
- Turn cell off when done: YES

Figure F2: Experimental Set-up for Figure F1

F2

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